5.1 Over view of Cyclic Voltammetry

The electrochemical investigation of coordination compounds started early after the discovery of polarography in the quarter of the last (20th) century. Over the past couple of decades potentials sweep techniques, such as Cyclic Voltammetry (CV), have been applied to an ever-increasing range of systems, and at the same time the mathematical description of these techniques has been developed sufficiently to enable kinetic parameters to be determined for a wide variety of mechanisms. It is, however, in the area of preliminary mechanistic investigations that sweep techniques, in particular Cyclic Voltammetry, are probably most useful. Cyclic Voltammetry, (CV) has become increasingly popular in all fields of chemistry as a mean of studying redox states. It is one of the electro analytical techniques, which has become a popular tool in recent years. Organic chemists have applied the technique to the study of biosynthetic reaction pathways1 and to the studies of electrochemically generated free radicals2. An increasing number of inorganic chemists have been using to study the effects of ligands on the oxidation/reduction behaviour of the central metal ion in complexes3. This type of information plays an integral role in many of the approaches directed towards solar energy conversion4 and in model studies of enzymatic catalysis5. CV can rapidly locate the electrode potential at which a drug, a metal ion or some other compound undergoes reduction or oxidation.

The basic principle and instrumentation involved in CV techniques were described by several books and review articles.(6-14) Here the potentials of working electrode is varied as a function of time and the resulting current is measured. A triangular waveform as shown in the Figure 5.1(a) is applied to the
Figure 5.1 Cyclic Voltammetry
(a) Triangular wave form
(b) Current-voltage Curve (Cyclic Voltammogram)
electrochemical cell. The potential of working electrode varies linearly in one
direction and at any selected potential the direction of the scan is reserved. The
switching time, \( t \), is decided by the nature of the reaction at the electrode and the
information desired. The current-voltage curve recorded as a result of this sweep
shows a peak when there is an electrochemical process-taking place at the
electrode as shown in Figure 5.1(b). The peak potential \( (E_{pa} \text{ or } E_{pc}) \) and the current
\( (i_{pc} \text{ or } i_{pa}) \) are the important tools in assessing the redox behaviour.

5.2 Electrochemical system components

To understand the experimental situation it is customary to know the
materials and properties of individual electrochemical system components. The
brief discussions of such components are as follows.

(a) The Solvent:

A number of physicochemical properties must be considered while
choosing a solvent for electrochemical work: (i) it must be a liquid at room
temperature, (ii) it must have sufficient solubility for ionic substances to form
conducting electrolyte; it must be able to dissolve the electroactive species of
interest, (iii) it must have a wide enough potential region for the study of the redox
process of interest, that is, the solvent itself must not undergo oxidation or
reduction in this potential region, and (iv) it must possess the required acid-base
properties.\(^{15-17}\) The cheapest solvent is water

A few detailed discussions of the solvents used in electrochemistry are
available which possesses many physicochemical properties. It can dissolve ionic
components and form highly conducting solutions. Many compounds of
electrochemical interest dissolve easily in the solvent. Its acid-base properties are
also well understood. However, the solvent itself gets reduced or oxidized to \( \text{H}_2 \)
and \( \text{O}_2 \) very easily. Hence it only possesses a potential region of 2.0 V for the
study of other processes. It react so well with radicals that it is unsuitable for
radical ion studies. Water is also easily forms oxide films on solid electrodes and hence affects reactivity and reproducibility. Some organic reactants are also soluble in water. This defect is normally overcome by using alcoholic mixed solvents or alcoholic stock solutions of reactants.

Acetonitrile is perhaps a solvent with inert electrochemical properties. It has +3.0 V (SCE) cathodic limits. Even these limits are probably set by the supporting electrolyte oxidation and impurity (water) reduction. If impurities are absent, radical ion chemistry may be studied very well. However, this solvent has very poor solubility for ionic species. Salts containing organic ions such as tetraalkyl ammonium salts must be employed. A few electroactive salts such as Ag(I) and Tl(I) salts are also soluble.

Dimethylformamide (DMF) is one of the aprotic solvents, which has very good dissolving power for ionic species. It has a cathodic limits upto –3.0 V anion radicals. Hence, this is the solvent of choice for studies on anion radicals and dianions. In the positive regions above +1.0 V the solvent itself decomposes. Cation radicals are less stable in the medium.

Dimethyl sulphoxide has electrochemical properties similar to DMF in the cathodic region. It has somewhat better anodic potential limits. Since it is not as basic as DMF, cation radicals are somewhat stable in this medium.

Methylene chloride is the solvent of choice for organic oxidation studies. It is stable upto +3.0 V as acetonitrile. Cation radicals and dications are quite stable in this medium. However, at negative potentials of –1.0 V, the solvent decomposes. The anionic species are less stable in this medium.

A host of other solvents are in voltammetric studies. Propylene carbonate widely used in voltammetric studies. Propylene carbonate widely used in battery research can, for example, stabilize both anion and cation radicals. Hexamethylene phosphorylamide may be employed for solvated electron studies. Tetra-hydrofuran is employed to study hardly reducible species. Even totally non-polar solvents
such as benzene and other hydrocarbons may be used to study the solution phase\textsuperscript{18} as well as surface\textsuperscript{19,20} processes. More detaileds of their properties and uses have already been reviewed.\textsuperscript{15-17}

\textbf{(b) Supporting Electrolytes :}

Here all ionic salts or ionizable compounds in a solvent are defined as the supporting electrolytes. It is very important to realize that they can influence the electrochemical process in a number of ways; (i) these electrolyte impart conductivity to the solvent and hence enable the continuous current flow in solution; (ii) they must remain electroinactive in the potential region of interest if any useful voltammetric study is to be conducted; (iii) if the concentration of the supporting electrolytes is very low, they can form a space charge near the surface and the space charge potential can influence the charge transfer kinetics; (iv) if the ions of the supporting electrolytes are adsorbed on the surface, they can catalyze or inhibit other reactions; (v) small cations may form ion pairs with the anion radicals formed in the electrode process and the properties of the ion pairs can be very different from those of the free anion radical; (vi) some ions may form complexes with the reactants and/or products; (vii) the supporting electrolyte generally control the acidity of the ionic solution; (viii) the liquid electrolyte melts and solid electrolytes act as the medium for the ionic phase; (ix) in a few circumstances such as oxide growth in alkaline media, they may function as the electroactive species.

Even today a number of voltammetric results at very positive potentials in KCl media is interpreted without possible influence of Cl\textsuperscript{-} adsorption. Reductions in Li\textsuperscript{+} salt solutions are interpreted without consideration of ion-pair effect. One must always consider all possible influences of supporting electrolytes if such pitfalls are to be avoided.

HClO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4} or HCl are normally employed for studies in acidic aqueous solutions; and NaOH or KOH are employed for alkaline media. In the neutral
region, if buffering is important, acetate citrate and phosphate buffers are usually employed. If the redox process does not involve acid base reactions, no buffers are needed and any electrolyte may be used. Alkali metal salts are usually employed.

A number of anions such as Cl\(^-\), OH\(^-\), citrate, tartrate and oxalate added to control acidity may also involved in complex formation as mentioned above. Some electrolytes such as KCN, KCNS and EDTA may intentionally be added to promote complex formation.

Solubility is the main consideration in selecting supporting electrolytes for aprotic solvents. LiClO\(_4\) is quite soluble in a few aprotic solvents. NaClO\(_4\) is much less soluble. A number of tetra-alkyl ammonium (TAA) salts show good solubility in aprotic media. Tetra-ethyl ammonium (TEA) and more recently tetra-n-butyl ammonium (TBA) salts are widely employed for this purpose.

Perchlorate ions are usually oxidized at about +1.6 V. BF\(_4^-\) ions are not oxidizable at least up to +3.0 V. This is the anion of choice in most recent works. PF\(_6^-\) has been introduced recently.

A number of molten electrolyte systems have been characterized. Lewis acid-base characteristics may be varied conveniently by varying the electrolyte composition. A recent work\(^{21}\) describes the properties and practices of a number of molten salt systems including room temperature melts.

**(c) The Reference Electrodes:**

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 are a number of electrode reactions, which possess the physicochemical properties\(^{22-24}\)

The standard reference electrode system is the reversible hydrogen where H\(^+\) ions and H\(_2\) gas are present in an electrolytic half cell with a platinum back
electrode. The electrode potential at unit activity of H\(^+\) and H\(_2\) at 25 °C is taken as the zero point for the electrochemical scale of potentials. This is the best electrode for the processes where H\(^+\), H\(_2\) or OH\(^-\) ion is the reactive species. The pH-dependence of the working and the reference electrodes will then be directly related.

The metal/metal ion electrodes may also be employed as reference electrodes. Cu/Cu\(^2+\) reference electrodes are extensively employed. Ag/Ag\(^+\) (acetonitrile) is used as the reference electrodes in non-aqueous media. Al/Al\(^3+\) reference electrodes are employed for measurements in non-polar solvents\(^{20}\) and in molten salt media.\(^{25,26}\)

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 Hg\(_2\)Cl\(_2\) /KCl paste which then is in contact with a saturated KCl solution. The electrode reaction is Hg\(^+\)/Hg reaction but because of the low solubility of Hg\(_2\)Cl\(_2\) the electrode potential depends on Cl\(^-\) concentration. The electrode potentials of such electrodes can very easily be maintained at a constant value. The Hg/Hg\(_2\)SO\(_4\), Ag/AgCl and Hg/HgO electrodes also belong to this group.

A film of redox material (say ferrocene/ferrocinium couple) may be produced on an inert electrode material by, say, polymerization. Such redox film electrode can function as a very good reference electrode.

(d) The Working Electrodes:

For practical convenience, one may classify the working electrodes into four types: (i) inert electrodes, (ii) reactive electrode, (iii) photo excitable or semiconductor electrodes, and (iv) synthesized or chemically modified electrodes. Overlap is very common in this classification. For example depending on the
potential region, one electrode may function either as inert or reactive electrode. This limitation need not however, restrict one from a convenient discussion of working electrodes employed in electrochemistry.

Inert electrodes, which do not chemically and electrochemically react in the potential region of interest, are the most often sought after electrodes for the study of solution phase reactions. Hg is the most popular electrode of this type\textsuperscript{27}. Absence of surface defects (liquid electrodes), easier cleaning procedures, and high cathodic overvoltage for hydrogen evolution are factors in its favour.

Since it easily dissolves anodically, Hg is not suitable in anodic regions. For such processes Pt is the electrode of first choice. In aqueous solutions an oxide film is formed in the anodic region and hydrogen evolution limits the cathodic potential region. In non-aqueous solvents, however, Pt provides a very wide potential region. Polycrystalline materials are often employed\textsuperscript{28,29}, but some recent works consider single crystal electrodes and their orientational effects. In aqueous media, Au offers a wider potential region when compared with Pt. Oxide formation takes place at much more positive potential. Polycrystalline as well as single crystal electrodes have been used.\textsuperscript{28}

A few other metallic inert electrodes such as boron nitrides and some carbides were introduced into electrochemistry.\textsuperscript{28} However, either because of poor reproducibility or high electrical resistivity, these electrodes were not very successful.

A number of carbon electrodes has been introduced into voltammetric studies.\textsuperscript{30,31} These electrodes have a very wide anodic as well as cathodic potential region, both in aqueous and non-aqueous solvents. Single crystal graphite materials are quite difficult to obtain and use. A few studies with such materials, however, indicate different behaviour in the basal plane containing the electron rings of graphite crystal and the edge plane which is perpendicular to it.\textsuperscript{32} Carbon paste made of graphite powder and a mineral solvent was one of the earliest inert
electrodes introduced into electrochemistry. Until recently pyrolytic graphite was widely used in voltammetry. Carbon fibres introduced recently may be considered as the miniature version of this graphite materials formed by pyrolysis and deposited on a mantle. It may also be formed as a film on other substrates. However, the vitreous or glassy carbon electrode introduced recently into electrochemistry is the most widely used carbon electrode material today. 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.

One may also employ chemically synthesized materials as the working electrodes. A great variety of such chemically modified electrodes are now available. Cyclic Voltammetry is extremely used for their preparation and characterization. These types of working electrodes can also catalyse a number of electrochemical reactions.

(e) Cells and other material components:

The simplest electrochemical cell can be a beaker with the three electrodes: (a) the working, (b) the reference, and (c) the auxiliary electrodes, dipping in an electrolyte solution. Oxygen or any other gaseous component in the atmosphere can contaminate this solution. Hence usually a glass cell with a ground joint is used. The ground joint cover has provisions for the three electrodes. There is also additional provision for removal of dissolved oxygen or other gases by passing an inert gas. The electrolyte volume of such a cell is around 25 ml. This is the most convenient cell design for non-aqueous solvents.

In the single component cell the working and auxiliary electrode compartments are not separated. In some situations the reaction products at auxiliary electrode may interfere with the reactants at the working electrodes. This is especially true if voltammetric experiments are carried out for longer times at slower sweep rates. For such purposes the working and the auxiliary electrode
compartments may be separated by mass transfer resistant materials such as glass frits. A third type of cell, which is becoming popular in recent times, is the thin layer cell.

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 auxiliary electrode does not complicate matters. It must not dissolve in the medium. The reaction product at the auxiliary electrode must reach or react at the working electrode. Pt electrodes fortunately meet most of these requirements and this is the most widely used auxiliary electrode in aqueous and non-aqueous as well as molten salt media. Pt 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 auxiliary electrode does not control the limiting current.

5.3 **Electrochemical Investigation of Cu(II) complexes of substituted Diphenylcarbazones.**

A detailed investigations on the cyclic voltammetric behaviour of transition metal complexes of a variety of organic ligands are reported in the literature.\(^{40-43}\) A thorough literature survey revealed that there are no reports on the Cyclic Voltammetric studies on transition metal complexes of substituted diphenylcarbazones. Hence, the present study is undertaken to understand the electrochemical behaviour of Cu(II) complexes of di(4-bromophenyl)carbazone, di(4-fluorophenyl)carbazone and di(4-methylphenyl)carbazone.

(a) **Experimental:**

The electrochemical experiments were carried out using potentiostat provided with the Data Acquisition PC interface card fabricated at Analytical Chemistry Division Bhabha Atomic Research Centre, Trombay, compatible with an IBM Personal Computer and coupled to a printer. The electrochemical cell
consists of a glass container with a cap having holes for introducing electrodes and nitrogen gas. The cell is then maintained oxygen free by passing nitrogen through the solution. A glassy carbon of was used as a working electrode and its potentials were measured with reference to Ag/AgCl. The platinum foil served as a auxiliary electrode. These electrodes are placed directly into the solution. Since the limiting (or peak) current in any type of voltammetry is temperature dependent, the cell is thermostated at the required temperature (298 K). In a typical cyclic voltammetric experiment, the cell (Figure 5.3) consisted of a solution of known concentration of the metal complex and supporting electrolyte Bu4NC1O4. A stream of nitrogen gas free from oxygen is passed through the reaction mixture which was previously thermostated. The three electrodes are connected to a computer-controlled potentiostat and required potential scan rate, initial potential, final potential and current sensitivity are set. The resulting current is measured as a function of applied potential.

**Pre-treatment of glassy carbon electrode**

Before each measurement, the glassy carbon surface was polished with fine emery sheet to 4/0 grade and then rinsed with purified water. The supporting electrolyte solution was placed in the cell and several potential sweeps were applied to obtain a low background. The compounds were then added and the first potential sweep was registered.
Figure 5.3 – Instrumental set-up for CV experiments

WE: Working electrode; RE: Reference electrode; AE: Auxiliary electrode
Table 5A. Cyclic Voltammetric data of Cu(II) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Scan rate (V/sec)</th>
<th>Epc (V)</th>
<th>Epa (V)</th>
<th>AEp (mV)</th>
<th>ipc (µA)</th>
<th>ipc /√v1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(D4BrPC)2]</td>
<td>0.05</td>
<td>-0.232</td>
<td>-0.149</td>
<td>83</td>
<td>6.74</td>
<td>30.14</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.254</td>
<td>-0.141</td>
<td>113</td>
<td>9.50</td>
<td>30.04</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.271</td>
<td>-0.119</td>
<td>152</td>
<td>13.51</td>
<td>30.21</td>
</tr>
<tr>
<td>[Cu(D4MPC)2]</td>
<td>0.05</td>
<td>-0.515</td>
<td>-0.434</td>
<td>81</td>
<td>7.40</td>
<td>33.09</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.520</td>
<td>-0.428</td>
<td>92</td>
<td>10.50</td>
<td>33.20</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.539</td>
<td>-0.422</td>
<td>117</td>
<td>14.89</td>
<td>33.29</td>
</tr>
<tr>
<td>[Cu(D4FPC)2]</td>
<td>0.05</td>
<td>-0.220</td>
<td>-0.142</td>
<td>78</td>
<td>5.42</td>
<td>24.24</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.228</td>
<td>-0.141</td>
<td>87</td>
<td>7.75</td>
<td>24.51</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.235</td>
<td>-0.137</td>
<td>98</td>
<td>11.06</td>
<td>24.73</td>
</tr>
</tbody>
</table>

(b) Electrochemical behaviour:

The redox activity of all the above copper complexes was studied in the potential range +0.2 to -0.8 V versus the ferrocene-ferrocenium redox system in acetonitrile (0.2 M Bu₄NClO₄, 298 K). They exhibit a well-defined voltammograms. No peaks corresponding to reduction have been observed down to -0.8 V, as the ligands were shown to be electrochemically inactive in the studied potential. The most significant feature of the above complexes is the couple Cu(II) to Cu(I). The analysis of the cyclic voltammetric responses with the scan rate varying from 0.05 to 0.2 V/sec. gives evidence for a quasi-reversible one electron reduction. Representative cyclic voltammograms are illustrated in Figure 5.31. The Table 5A summarizes the electrode potentials for the most significant redox change of the above complexes in acetonitrile. Also reported the difference between the forward and backward peaks, which if compared with the value of 63 mV for a purely reversible one-electron transfer, can provide a rough evaluation of the degree of reversibility of one electron addition. It is observed at a
Figure 5.31 - Cyclic Voltammogram of (a) \([\text{Cu(D4BrPC)}_2]\) (2 mM), (b) \([\text{Cu(D4MPC)}_2]\) (2 mM) and (c) \([\text{Cu(D4FPC)}_2]\) (2 mM), each at a scan rate of 0.1 V/sec.
scan rate of 0.05 V/sec., the complex \([\text{Cu(D4BrPC)}_2]\) exhibited a pair of cathodic at -0.232 V and anodic at -0.149 V peaks representing the Cu(II)/Cu(I) couple. The ratio of anodic to cathodic peak height was less than one, however its height increased with the increase in the square root of scan rate \((v^{1/2})\). The \(i_{pc}/v^{1/2}\) value for cathodic peak was 30.04 at 0.1 V/sec. and almost constant at other scan rates as illustrated in Table 5.4A, establishing the electrode process to the diffusion controlled. The typical plots are shown in Figures 5.32 (a and b).
Both peaks took broad shape as the scan rate increased. Besides, the cathodic peak shifted to more negative potentials while anodic peak to anodic potentials thus increasing the peak-to-peak separation ($\Delta E_p$) from 83 mV (0.05 V/sec) to 152 mV (0.2 V/sec) as shown in Figure 5.33. These characteristic features are consistent with the quasi-reversibility of Cu(II)/Cu(I) couple.\textsuperscript{44} Similarly the redox activities of other two complexes viz. [Cu(D4MPC)\textsubscript{2}] and [Cu(D4FPC)\textsubscript{2}] can be explained.

The cathodic potential shift is maximum in case of [Cu(D4MPC)\textsubscript{2}], minimum in [Cu(D4FPC)\textsubscript{2}] and in between values are observed for [Cu(D4BrPC)\textsubscript{2}]. The behaviour of these copper complexes in Cyclic Voltammetry is attributed to the electronegativity of the substituents on the para position of the phenyl nucleus, it is maximum for the complex having electron-withdrawing group eg. methyl group and minimum for the complex having electron withdrawing group on para position of the phenyl nucleus eg. fluoro group. For bromo group it is less negative than fluoro, the shift is in between that observed for the other groups.
Figure 5.32—Cyclic Voltammogram of [Cu(D4BrPC)₂] (2 mM) at Scan rates (a) 0.05, (b) 0.1 and (c) 0.2 V/sec.
References