CHAPTER-3

Material and Methods
3.1 Techniques for complexation with polarographic details

The stoichiometry of metal complexes is necessary, before, it can be used in biological processes, medicines, laboratories, industries, analysis etc. To predict the nature of unknown reaction and to explain its coordination behaviour, it is necessary to have the quantitative measurements on the degree of metal ligand dissociation. A number of methods employed for this purpose.

(a) Absorption spectra measurements\(^1\).
(b) Reflective index studies\(^2\).
(c) pH Measurements\(^3\).
(d) Nuclear magnetic measurements\(^4\).
(e) Raman spectra measurements\(^5\).
(f) Solubility methods\(^6\).
(g) Dialysis\(^7\).
(h) Reaction rates\(^1\).
(i) Magnetic moments measurements\(^8-10\).
(j) Amperometric titration methods\(^11\).
(k) X-ray studies\(^1\).
(l) Polarography\(^12,13\).

The polarographic technique, among all the above techniques for studying complexation, is the most convenient and suitable to study the complex formation in solution, therefore, it has been
decided to follow it in the present study to determine the complex formation between Zn(II) and Mn(II) with neomycin, chlortetracycline, oxytetracycline, tetracycline, penicillin-V, penicillin-G as primary ligands and phenacetin, aspirin, paracetamol as secondary ligands.

**Polarographic technique**

The polarographic technique, of analysis, was developed by Joroslav Heyrovsky\(^{14}\) in 1920 at the Charles University in Prague, is based on the current-voltage curve arising at the rate determining step in the electrochemical reaction\(^{12}\). In 1925, an instrument for polarography, which records dropping mercury electrode C.V. curves automatically in a small fraction of the time required to obtain them point by point, was invented by Heyrovsky and Shikata\(^{15}\). Kolthoff and Laitinen\(^{16}\) advocated the more descriptive general name “voltammetry” to indicate that voltage and current are the two quantities measured, the former providing qualitative information about nature of electroactive species present and the later providing quantitative indication of its concentration, but chemists became interested in it only after the publication in 1935-40\(^{17-22}\) of the theoretical basis underlying polarography.

In Polarography, a small amount of material is reduced or, less commonly, oxidized at a microelectrode in an electrolysis cell, which consists of dropping mercury electrode as the analytical microelectrode and a saturated calomel electrode as the reference electrode. This method involves, polarisation of the microelectrode. This condition results, when the cell current is no longer dependent
upon the equilibrium potential of the microelectrode but depends upon the diffusion rate of the reducible species in the test solution.

If a steadily increasing voltage is applied to a cell, it is possible to construct a reproducible current-voltage curve. The electrolyte is a dilute solution of the material under investigation in a suitable medium containing an excess of an indifferent electrolyte to carry the bulk of the current and raise the conductivity of the solution, thus ensuring that the material to be determined, if charged, does not migrate to the dropping mercury electrode. From an examination of current-voltage curve, information as to nature and concentration of material, may be obtained.

In the curve, a plateau region is obtained, where the cell current is proportional to the concentration of the reducible species in the solution under analysis.

Although, it, is the diffusion current of an electroactive substance in solution that gives the characteristic polarographic wave, there are other possible contribution to the total limiting current that may also influence the current-voltage curves. A small residual current, migration current and sometimes absorption and kinetic currents are the components of the observed limiting current. Therefore, it is necessary, to account for all current which contribute the true polarographic wave.

(a) **Residual current**

A current-voltage curve, for a solution of ions with strong negative reduction potential, indicates that a small amount of current flows before the decomposition of the solution begins. It is observed
that the current increases almost linearly, with the applied voltage even in the purest air free solution, which can not be due to reduction of impurities. It must, therefore, be considered non-Faraday or condenser current which depends upon the potential of dropping mercury, the area of mercury exposed per second (which in turn, depends upon the characteristics of the capillary) and the presence of capillary active substances in the solution. It is known that metal when submerged in an electrolyte is covered with an electrical double layer of positively and negatively charged ions. The capacity of double layer and hence charging current\textsuperscript{24,25} vary with upon the potential which is imposed upon the metal.

In practice, residual current, $I_r$, is greater than the condenser current, $I_c$, because it includes “Faradaic current”, $I_f$, due to reduction of traces of reducible impurities in the solution, so that,

$$I_r = I_c + I_f$$

It is also observe that minimum detectable concentration of a reducible substance will depend upon the accuracy of the residual current measured. It is, therefore, essential, in accurate polarographic work, to determine the residual current in the particular supporting electrolyte solution that is used whenever this is possible.

(b) *Migration current*

The fraction of the limiting current due to electrical migration of the reducible ions, was named “migration current” by Heyrovsky\textsuperscript{26}, is a consequence of electrical attraction between the electrode and oppositely charged ions. Electroactive material is able to reach on electrode by electrostatic attraction and also by diffusive forces,
but, in polarography, it, can reach the surface of the electrode only by diffusion. Hence, it is necessary to eliminate the migration current that can be done by adding an indifferent electrolyte whose concentration is so large that its ions carry essentially almost all the current. (An indifferent electrolyte only conducts the current but does not react with the material under investigation not at the electrodes with the potential range studied).

In practice, this means that the concentration of the added electrolyte (supporting electrolyte) must be atleast 100 times larger than that of the reducible ions to eliminate completely the migration current.

(c) Diffusion current\textsuperscript{27}

To neutralize the electrical force on the reducible (or oxidizable) ion, an excess of supporting electrolyte is present in the solution. This is due to reason that the ions of added salt carry practically all the current and the potential gradient is compressed or shortened to a region so very close to the electrode surface that it no longer operates to attract the electroactive ions, the limiting current, under these conditions, is called diffusion current. The polarographic diffusion current was first calculated by Ilkovic\textsuperscript{28-30}, in terms of diffusion species and of growing mercury drop :

\[ i_d = 607nD^{1/2} \cdot c \cdot m^{2/3} \cdot t^{1/6} \] \hspace{1cm} (1)

In above eq.

\[ i_d = \text{diffusion current}. \]

\[ n = \text{number of faradays of electricity required per mole of the electrode reaction}. \]
D = diffusion coefficient of ions in cm$^2$ sec$^{-1}$.

$ c = \text{concentration in milli mol litre}^{-1}. $

$m = \text{rate of flow of mercury from the dropping electrode}$

$ \text{capillary in mg sec}^{-1}. $

$t = \text{drop time in seconds, usually measured at the half wave}$

$ \text{potential.}$

From above equation, it follows that "the observed diffusion current is directly proportional to the concentration of electroactive species. Which is the basis of quantitative analysis." The Ilkovic equation does not take into consideration the curvature of the electrode.

Therefore, Lingane and Loveridge gave a modified equation, for accurate practical work, as -

$$ i_d = 607nD^{1/2} \cdot c \cdot m^{2/3} \cdot t^{1/6} \cdot [1 + 39(D^{1/2}t^{1/6}/m^{1/3})] \ldots \ldots (1.1) $$

This modified equation correctly expressed the dependence of $i_d$ upon 'm' and 't' within the experimental error.

The diffusion current is affected by temperature, the concentration of electroactive species, dimensions of capillary, pressure on dropping mercury electrode, viscosity of the medium, composition of the base electrolyte and molecular or ionic state of electroactive species.

(d) **Polarographic maxima**

Some time when current voltage curve obtained with the dropping mercury electrode, polarographic maxima$^{23}$ are obtained, which are recognised by appearance of a sharp peak or rounded hump at the top of polarographic wave. Usually two types of maxima
are observed, that must be eliminated during the measurement of true diffusion current. This can be done by the addition of a very well quantity of a surface active substance such as dyestuff, gelatin, sodium perchlorate or other colloids. These suggested surface active substances from an absorbed layer on the aqueous side of the mercury solution interface which resists compression, this prevents steaming movement of the diffusion layer at the interface.

(e) Half wave potential

In polarography, each electroactive species is characterised by its half wave potential which is the potential found on the steeply rising portion of current voltage curve and it is one half of the distance between the residual current and final limiting current plateau. It may also be defined as the potential on the polarographic wave where the current is equal to one half of the diffusion current. It is denoted by $E_{1/2}$.

The half wave potential is related to the reduction taking place at the dropping mercury electrode which is represented as -

Oxidant + ne⁻ $\rightarrow$ Reductant

$E_{1/2}$, half wave potential, is related to the standard oxidation potential $E^0$ by the eq

$$E_{1/2} = E^0 - \frac{0.0591}{n} \log \left[ \frac{D_{\text{red}}}{D_{\text{ox}}} \right]^{1/2}$$

Where $D_{\text{red}}$ and $D_{\text{ox}}$ represent the diffusion coefficients of the appropriate reducing and oxidising species.

The ease of oxidation and reduction of a complex ion at the dropping mercury electrode is different from that of aquated metal
ion and half wave potential, obtained under such condition that the reaction are reversible have great significance in thermodynamic and may be related to ordinary standard potentials. If the reduction process of complex is reversible, the values of dissociation constants of the complex and the number of coordinated groups can be calculated\textsuperscript{32} from the change in half wave potential. Irreversibility of a process can easily be determined by this method\textsuperscript{33}.

**(f) Limiting current\textsuperscript{34,35}**

When all the oxidant reaching at the surface of dropping mercury electrode get reduced, a certain value of current is observed, called limiting current, which is independent of applied voltage. The region of curve, where the constant current flows, called limiting current plateau because it, represents the limiting or maximum rate at which the particuler ionic species can be discharged under the given experimental condition.

The only factor affecting the limiting current, if, the migration current is almost eliminated by the addition of sufficient electrolyte, is the rate of diffusion of electroactive material from the bulk of the solution to the electrode surface. Polarography is the first voltammetric technique to gain prominance and it is still the most extensively used due to its sensitivity, rapidity, wide concentration range, possibility to determine several species (quantitatively and qualitatively) in the same solution in the singal experiment and wide applicability for determination of substances, solid, liquids, or gases, organic and inorganic, ionic or molecular, that can be dissolved in a solvent of reasonable dielectric constant and either reduced or oxidized at the
dropping mercury electrode.

Amperometric titration is also closely related to polarography. The concentration range in polarography is generally regarded to $10^{-2}$ to $10^{-5}$ M. Above $10^{-5}$ M maxima are encountered and migration current may not be eliminated.

Below $10^{-5}$ M residual current are much longer than Faraday current. A precision of ± 3% to 5% is readily attainable at concentration range between $10^{-2}$ to $10^{-5}$ M. However with addition efforts and care to maintain the experimental condition constants, e.g. temperature, solution, composition, capillary characteristics and the potential, a precision approaching ± 1% can be obtained.

3.2 **Polarographic behaviour of metal ions**

The polarographic behaviour of metal ions, is most important approach to determine its quantitative, qualitative analysis and also to study the complex formation with any selected complexing agent in a suitable medium under appropriate condition, consists of current-voltage curve during its reduction at the d.m.e. and the determination of fundamental polarographic characteristics.

When the reduction or oxidation of the metal ion complex takes place reversibly at the dropping electrode, some quantitative information can be made. Therefore, it is necessary to establish reversibility of the electrode reaction in any given case before attempting to draw quantitative conclusions from the experimental data.

The three types of electrode reactions involving complex metal ion, are -
(a) Reversible electrode reaction
(b) Quasireversible electrode reaction
(c) Irreversible electrode reaction

(a) **Reversible electrode reaction**

It is shown by the theory of current-voltage curve that the electron transfer on the plateau of the curve is so fast that the ions or molecules of the electroactive substances reduced or oxidised as rapidly as they arrive or are formed at the electrode surface.

As the potential moves from the plateau of the C-V curve towards its foot, the rate of electron transfer process decreases and the reduction or oxidation becomes less and less complete. A true reversible reaction is so rapid that the thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential and the variations of current with potential reflect the changing position of the equilibrium and is given by the Nernst’s equation. But in practice, no electrode reaction is so fast than equilibrium is actually attained at every instant, therefore we can say that a electrode reaction is reversible, if, within the limit of experimental error, its behaviour can not be distinguished from that of an infinitely fast reaction.

For these reactions, the plots of $E_{de}$ vs log $(i_d - i) / i$ should be straight line\textsuperscript{36-38} whose intercepts give the value of $E_{1/2}$ and slopes give the value of 0.0591/n.

The diffusion controlled nature of the waves is confirmed from the plots between $i_d$ vs $\sqrt{h}$ obtained a straight line passing through the origin.
(b) Quasi reversible electrode reaction

The electrode reactions which involve reversible electron transfer step, are followed by a slow chemical transformation is given as follows

\[ A \pm ne = B \text{ (reversible)} \text{ and} \]

\[ B \rightarrow C \text{ (slow)} \]

These reactions are called quasireversible reactions\textsuperscript{36}. In these reaction, the plots between \( \log \left( \frac{i_d - i}{i} \right) \) against \( E_{de} \) obtained are slightly curved rather than straight lines\textsuperscript{39,41}. The values of \( \epsilon \)'s, \( E_{1/2}^{\text{rev}} \), \( \alpha \) and \( \gamma \) can be calculated by using modified Gelling's method\textsuperscript{40,41}. The equations are -

\[ E_{1/2}^{\text{rev}} = E_{d,e} - \frac{RT}{nF} \log \left[ \frac{i_d - i}{i} \right] \]

and

\[ i \rightarrow 0 \quad \log (Z-1) = \log \frac{1.13}{\lambda \sqrt{t_d}}(1-\alpha) \frac{nF}{2.303RT} (E - E_{1/2}^{\text{rev}}) \]

If \( E_{de} \) is plotted against \( \log \left( \frac{i_d - i}{i} \right) \), a curve obtained is extrapolated to \( i \rightarrow 0 \), give the values of \( E_{1/2}^{\text{rev}} \). The plots of \( \log (Z-1) \) vs \( E - E_{1/2}^{\text{rev}} \) give straight lines and from the slopes and intercepts of these plots, the value of \( \alpha \) and \( \epsilon \)'s can be calculated. The meanings and symbols used were given in references\textsuperscript{40,41}. Some references in this regard were also available in the literature\textsuperscript{42-44}.

(c) Irreversible electrode reaction

The electrode reactions which are very slow and proceed on a fraction of the way towards equilibrium during the life of each drop, are classified as irreversible reactions. For an irreversible wave, the
kinetic parameters, viz \( \alpha, \lambda, \epsilon \) can be calculated by Koutecky's method\(^{45,46} \) as extended by Meites\(^{36} \), which is based on a plot of \( E_{d.e.} \) vs \( \log i / (i_d - i) \) and may be constructed for irreversible waves.

The value of kinetic parameter can be calculated by -

\[
E_{d.e.} = E_{1/2} - \dfrac{0.0542}{\alpha n} \log \left[ \dfrac{i}{i_i} \right]
\]

and

\[
E_{1/2} = -0.2412 - \dfrac{0.0591}{\alpha n} \log \left[ \dfrac{1.349 K^O_{i_b} t^{1/2}}{D^{1/2}} \right]
\]

where the symbols have their usual meanings given in reference\(^{45,46} \).

In the above equation, if \( E_{d.e.} \) is plotted against \( \log i / (i_d - i) \), a straight line obtained with the slope of -0.0542/n and intercept of \( E_{1/2} \), and with the help of \( \alpha, n, E_{1/2} \) and \( D^{1/2} \) (calculated by Ilkovic equation), the value of \( \epsilon \) can be calculated. The various criteria for the determination of reversibility of current-voltage curves were given in literature\(^{36,39} \).

Reversible electrode process is very fast while quasi reversible and irreversible process are slow. The nature of process is determined by the value of rate constants as-

\( \epsilon > 2 \times 10^{-2} \text{ cm sec}^{-1} \rightarrow \text{Reversible} \)

\( \epsilon \to 2 \times 10^{-2} - 3 \times 10^{-5} \text{ cm sec}^{-1} \rightarrow \text{Quasi reversible} \)

\( \epsilon < 3 \times 10^{-5} \text{ cm sec}^{-1} \rightarrow \text{Irreversible} \)

The nature of electrode process can also be obtained by using the following relation

\[
E_{3/4} - E_{1/4} = -\dfrac{0.0591}{n}
\]
If the slope of a polarographic wave satisfies above equation then it confired that the process is reversible. If not, then it shows that the process is not reversible.

3.3 Determination of stoichiometry and stability constants

Various methods$^{40,41,45,46,47-52}$ are used to determine the complex formation and also to determine the values of kinetic parameters of electrode reactions and stability constants of complexes. The determinations depend upon the nature of current-voltage curves of metal and complexes. Here few method are given for the same.

(a) Lingane's method$^{53}$

This method is based on the fact that the reduction potential of metal ions and their complexes are usually shifted to more negative values as a result of complex formation. The diffusion current changes and usually becomes smaller$^{51}$.

Consider the reduction of a complexed ion in the metallic state (as an amalgam) at the dropping mercury electrode. The electrode reaction may be expressed as

$$MX_j^{(n+pm)} + ne^- + Hg \rightleftharpoons M(Hg) + j(X)^m$$  \hspace{1cm} (2.1)

where $MX_j$ is the complex of metal ion $M$ with ligand $X$ carrying a charge $(n-jm)$, the charges on metal and ligand species being $n^+$ & $m^-$ respectively, consider the following equilibrium-

$$MX_j^{(n+pm)} \rightleftharpoons M^{n+} + jX^m$$  \hspace{1cm} (2.2)

$\text{I} \ne, E^0$

$M$
If these processes take place reversibly and much more rapidly than the rate of natural diffusion of ions to the electrode surface then the potential of the d.m.e. at all points on the polarographic wave, may be given by.

$$E = E^0_A - \frac{RT}{nF} \ln \frac{C_A^0 \nu_A^0}{C_M^0 \nu_M^0} \quad \text{(2.3)}$$

where $C_A^0$ is the concentration of amalgam formed on the surface of the d.m.e., $\nu_A^0$ its activity coefficient, $C_M^0$ is the concentration of the metal ion. The $\nu_M^0$ the activity coefficient, $E^0_A$ is the standard potential of the amalgam. The overall thermodynamic stability constant, $\beta_{MX}$, of complex $MX$ (charges are now omitted for clarity) is given by

$$\beta_{MX} = \frac{[MX]}{[M][X]} \quad \text{(2.4)}$$

where, the terms in brackets represent activities. The concentration of the complex in the bulk of the solution, for a given concentration of metal ion and ligand, may then be written as:

$$C_{MX} = \frac{\beta_{MX} C_M \nu_M [X]}{\nu_{MX}} \quad \text{(2.5)}$$

At the electrode surface, the metal ion will have a concentration given by

$$C_{MX}^0 = \frac{\beta_{MX} C_M^0 \nu_M [X]}{\nu_{MX}} \quad \text{(2.6)}$$

Where superscript o refers to values at the surface. Equation (2.6) is valid, if, it is to be assumed at the concentration of ligand is
large and constant throughout the solution with the same value of activity coefficient both in the bulk and at the electrode surface. It is now possible to substitute for \( C_m^o \) from equation (2.6) into equation (2.3) to give

\[
E = E_A^o - \frac{RT}{nF} \ln \frac{C_m^o \nu_m^o \beta \nu_m [X]^j}{\nu_{mxj} C_{mxj}^o} \tag{2.7}
\]

If the complexed ions arrive at the electrode by diffusion only, the mean current at any point of the reduction wave may be given by:

\[
i = K I_{mxj} (C_{mxj} - C_{mxj}^o) \tag{2.8}
\]

where \( K \) and \( I_{mxj} \) are the capillary constants (m^2/3 t^1/6) and (607 nD^1/2) is the diffusion current constant of the species \( MX_j \). When \( C_{mxj}^o \) approaches zero, the value of limiting current is given by:

\[
i_d = K I_{mxj} C_{mxj} \tag{2.9}
\]

A similar relation is obtained in terms of concentration of metal atoms within the mercury i.e.

\[
i = K I_A C_A \tag{2.0}
\]

where \( I_A \) is the diffusion current constant of metal atoms in the amalgam. Thus substitution for \( C_A^o \) from equation (3.0) into equation (2.7) we get

\[
E = E_A^o - \frac{RT}{nF} \ln \frac{\nu_A^o \beta \nu_A [x]^j}{K I_A \nu_{mxj} C_{mxj}^o} \tag{3.1}
\]

from equation (2.8)

\[
K I_{mxj} C_{mxj}^o = K I_{mxj} C_{mxj} - i = i_d - i \text{ by equation (2.9)}
\]
so that

\[ C^0_{MXj} = \frac{(i_d - i)}{K_{I_{MXj}}} \]  \hspace{1cm} (3.2)

substitution for \( C^0_{MXj} \) in equation (3.1) gives

\[ E = E_A^0 - \frac{RT}{nF} \ln \frac{i_{\beta_{MXj}}}{I_A} \frac{K_{I_{MXj}}}{(i_d - i)} \frac{\beta_{MXj}[x]}{v_{MXj}} \]  \hspace{1cm} (3.3)

\[ E = E_A^0 - \frac{RT}{nF} \ln \frac{K_{I_{MXj}}}{I_A} \frac{\beta_{MXj}[x]}{v_{MXj}} \]  \hspace{1cm} (3.4)

Then equation (3.4) becomes

\[ (E_{1/2})_e = E_A^0 - \frac{RT}{nF} \ln \frac{\beta_{MXj}[x]}{v_{MXj}} \]  \hspace{1cm} (3.5)

and the \( E_{1/2} \) of simple metal ion is

\[ (E_{1/2})_e = E_A^0 - \frac{RT}{nF} \ln \frac{\beta_{MXj}[x]}{v_{MXj}} \]  \hspace{1cm} (3.6)

Hence, the shift in \( E_{1/2} \), due to the presence of an excess of ligand, \( X \), is given by:

\[ (E_{1/2})_e - (E_{1/2})_c = \Delta E_{1/2} = 2.303 \frac{RT}{nF} \log \frac{\beta_{MXj}[x]}{v_{MXj}} \]  \hspace{1cm} (3.7)

If, diffusion current constant of metal is equal to the diffusion current constant of complexes i.e. \( l_{M}=l_{MXj} \) then the concentration of free ligand, \([x]\), may be equal to the analytical concentration, \( C_X \), and the activity coefficients may be dropped i.e. \( V_M[X]^i/V_{MXj} \approx 1 \), then equation (3.7) may be expressed in simplified form originally used by Lingane\(^{52}\) viz.,

\[ \Delta E_{1/2} = 2.303 \frac{RT}{nF} \log \beta_{MXj}^{i} C_X^{i} \]  \hspace{1cm} (3.8)

\[ \Delta E_{1/2} = \frac{0.0591}{n} \log \beta_{MXj}^{i} + \frac{0.0591}{n} \log C_X (at 25^\circ C) \]  \hspace{1cm} (3.8)
It is clear from the equation (3.4) and (3.5) that

\[ E = (E_{1/2})_c - \frac{0.0591}{n} \log \left( \frac{i}{i_a - i} \right) \text{ (at 25°C)} \quad (3.9) \]

Equation (3.5) further predicts that \( E_{1/2} \) is independent of the concentration of complexed species and can further be simplified and written as,

\[ (E_{1/2})_c = E^0_A - \frac{0.0591}{n} \log \beta_{MX_j} - \frac{0.0591}{n} \log C_x \quad (4.0) \]

It is clear that the rate of change of half wave potential with ligand concentration may be expressed as,

\[ \frac{d (E_{1/2})_c}{d \log C_x} = -j \frac{0.0591}{n} \text{ (at 25°C)} \quad (4.1) \]

Thus, a plot of \((E_{1/2})_c\) vs \(\log C_x\) should be linear with slope \(-j(0.0591/n)\), from which the coordination number, \(j\) of the complex, \(MX_j\), may be determined. If \(j\) is known, it is then a simple matter to calculate \(B_{MX_j}\) from equation (3.8). This method has great importance in complex formation. When a series of complex is formed, DeFord and Hume method\textsuperscript{53} is applied.

(b)\textsuperscript{54} DeFord and Hume method

This method is applied when the system involves consecutive formed complex ions in solution. The principle of this method is the same as discussed in the Lingane’s method. For complex ion of a metal which is soluble in mercury, the reduction to the metallic
state (amalgam) at the dropping mercury electrode may be represented by:

\[ \text{MX}_i^{(n-b)} + \text{ne} \rightleftharpoons \text{M}_{\text{amalgam}} + jX^b \quad \text{(4.2)} \]

where \( X^b \) is the complex forming substance for convenience, this reaction may be regarded as the sum of the partial reactions.

\[ \text{MX}_i^{(n-b)} \rightleftharpoons \text{M}^{n+} + jX^b \quad \text{(4.3)} \]

and

\[ \text{M}^{n+} + \text{ne} \rightleftharpoons \text{M}_{\text{amalgam}} \quad \text{(4.4)} \]

where \( \text{M}^{n+} \) symbolize the simple metal ions. If the electrode reactions are reversible, then the potential of the dropping mercury electrode is given by,

\[ E_{\text{d.e.}} = E_{\text{a}} - \frac{RT}{nF} \ln \frac{C_{a}^{0} f_a}{C_{M}^{0} f_{M}} \quad \text{(4.5)} \]

where \( C_{a}^{0} \) is the concentration of the amalgam at the electrode surface. \( C_{M}^{0} \) is the concentration of simple metal ions at the electrode surface and the \( f \)’s are the corresponding activity coefficients. Since the amalgams formed at the electrode surface are very dilute, \( f_a \) may be considered to be unity and will be neglected here after.

If the formation of the complex ions is rapid and reversible then for each individual complex

\[ C_{\text{MX}_i^{(n-b)}} = K_j C_{M} f_{M} (C_{X_i} f_{X_i}) \quad \text{(4.6)} \]

where \( K_j \) is the formation constants of the complex \( \text{MX}_i^{(n-b)} \). \( C_{\text{MX}_i} \) is the concentration of the complex in the body of the solution, \( C_{M} \) is the concentration of the simple metal ion in the body of the solution,
$C_X$, is the concentration of the complex forming substance, and the 
'f's are the corresponding activity coefficients. Also,

$$C_{MX_i} f_{MX_i} = K_i C_X^o f_m (C_X^i (f_X)^i)$$

where $0$ superscripts show the concentrations at the electrode sur-
face. On rearranging equation (4.7) we get

$$C_m^o f_m = \frac{\Sigma C_{MX_i}^o}{\Sigma \frac{K_i (C_X^i) (f_X^i)}{f_{MX_i}}}$$

Combination of equation (4.5) and (4.7) gives

$$E_{de} = E_a^o - \frac{RT}{nF} \ln C_a^o \frac{\Sigma \frac{K_i (C_X^i) (f_X^i)}{f_{MX_i}}}{\Sigma C_{MX_i}^o}$$

If an excess of supporting electrolyte is present to eliminate the 
migration current, the current at any point on the wave is given by

$$i = \Sigma j = K \Sigma I_j (C_{MX_j} - C_{MX_j}^o)$$

where $K$ is the capillary constant $m^{2/3}t^{1/6}$ and $I_j$ is the diffusion current 
constant $607nD^{1/2}$ of the complex $MX_j$. From equation (4.6), (4.7) 
and (5.0). We get

$$i = Ki_c \Sigma (C_{MX_j} - C_{MX_j}^o)$$

where $I_c$ is the apparent diffusion current which is related to the indi-
vidual $I_j$ values

$$I_c = \frac{\Sigma \frac{K_i (C_X^i) (f_X^i)}{f_{MX_i}}}{\Sigma \frac{K_i (C_X^i) (f_X^i)}{f_{MX_i}}}$$

Similarly, the diffusion current is given by

$$i_d = Ki_c \Sigma C_{MX_j}$$
The concentration of the amalgam at the electrode surface is related to the current by:

\[ i = K I_m C_a^0 \]  

(5.4)

where \( I_m \) is the diffusion current constant of metal. Combination of equations (4.9), (5.1), (5.3) and (5.4) shows that the half wave potential of the reducible ion in the presence of the complex-forming substance is given by

\[ (E_{1/2})_c = E_a^0 - \frac{RT}{nF} \ln \frac{I_c}{I_m} \sum \frac{K(C_i^j)(f_i^j)}{f_{ix_i}} \]  

(5.5)

and \((E_{1/2})_s\) of metal is given by

\[ (E_{1/2})_s = E_a^0 - \frac{RT}{nF} \ln \frac{I_s}{I_m} \]  

(5.6)

The half wave potential of simple metal ion when its activity coefficient is unity, is given by

\[ (E_{1/2})_s = (E_{1/2})_s - \frac{RT}{nF} \ln f_s = (E_a^0) - \frac{RT}{nF} \ln \frac{I_s}{I_m} \]  

(5.7)

Combination of equation (5.5) and (5.7) gives on rearrangement

\[ F_0[X] = \sum \frac{K C_i^j f_i^j}{f_{ix_i}} = \text{antilog} \left[ 0.435 \frac{nF}{RT} \left\{ \left( \frac{(E_{1/2})_s - (E_{1/2})_c}{(E_a^0) - (E_a^0)} \right) \right\} + \log \frac{I_s}{I_c} \right] \]  

(5.8)

where the symbol \( F_0[X] \) is introduced for convenience to represent the experimental measurable quantity on the right hand side of the equation. The function \( F_1[X] \) is defined by the relation:

\[ F_1[X] = \left\{ F_0[X] - \frac{K}{f_a} C_x f_x \right\} \]  

(5.9)

where \( K \) is the formation constant of the zero complex which is of course unity. If \( F_1[X] \) is plotted against \( C_x f_x \) and is extrapolated to \( C_x = 0 \), it is apparent that the value of \( F_1[X] \) at the intercept is equal to \( K f_a \). Similar the function \( F_2[X] \) ....... \( F_N[X] \) may be calculated to
find out the values of $K_2, K_3, \ldots, K_N$, the consecutive formation constants of the complexes. If $F_1[X]$ vs $C_x f_x$ plot for the last complex is straight line, parallel to the concentration axis, it means, the complex formation has been stopped. Further, this method has been modified by Irving.

(C) **Schaap and McMaster method**:

In 1961, Schaap and McMaster developed a logical extension of the DeFord and Hume method by applying the later to cases where metal ions form complexes with two ligand species simultaneously in solution. Consider the equilibrium of the following type

$$M + iX + jY \rightleftharpoons MX_i Y_j \quad \text{(6.0)}$$

where $i$ and $j$ are the stoichiometric numbers and $X$ and $Y$ are two different ligand species, the DeFord and Hume type $F_0[X]$ function may be extended to give a new function. $F_{oo}[X,Y]$ expressed in the form:

$$F_{oo}[X,Y] = \sum_{0}^{N} \beta MX_i Y_j[X][Y] \quad \text{(6.1)}$$

where activity coefficients have been ignored. As before the $F_{oo}[X,Y]$ function is given by

$$F_{oo}[X,Y] = \text{antilog} \left( -\frac{0.434nF}{RT} \Delta E_{1/2} + \log \frac{I_s}{I_c} \right) \quad \text{(6.2)}$$

For the simple case where a maximum of the bound ligand of type $X$ and $Y$, occurs, factorization of the $F_{oo}[X,Y]$ function leads to:

$$F_{oo}[X,Y] = \{ \beta_{oo} + \beta_{o1}[Y] + \beta_{o2}[Y]^2 + \beta_{oo2}[Y]^3 \}[X]^0 + \{ \beta_{10} + \beta_{11}[Y] + \beta_{12}[Y]^2 \}[X] + \{ \beta_{20} + \beta_{21}[Y] \}[X]^2 + \{ \beta_{30} \}[X]^3 \quad \text{(6.3)}$$

Here $[Y]$ is regarded as maintained constant while $[X]$ is varied. From the equation (6.3) the $\beta_{11}$, $\beta_{12}$ and $\beta_{21}$ may be calculated.
3.4 Determination of kinetic parameters

In this determination, following methods are used:

(a) Gelling's method

If electroactive species reaches slowly at d.m.e. then, this method followed by Tamamushi and Tanaka\textsuperscript{40,41} are used to determine the values of \((E_{1/2})_{\text{reversible}}\) and also to calculate the kinetic parameters viz., \(\zeta, \alpha\) and \(\lambda\). The value of \(D\) can be calculated by Ilkovic equation. If \((E_{1/2})_{\text{reversible}}\) is known at the concentration of ligand. Then stability constant of ternary complex can be obtained by using Schaap and McMaster method\textsuperscript{55}. The values of \(\zeta, \alpha\) and \(\lambda\) can be obtained by the following equation:

\[
\log (Z - 1) = \log \frac{1.13}{\lambda \sqrt{t_d}} - (1 - \alpha) \frac{nF}{RT} [E - E_{1/2}] \quad (6.4)
\]

If \(\log (Z-1)\) is plotted against \((E-E_{1/2})\), a straight line is obtained whose intercept is \(\log \left(\frac{1.13}{\lambda \sqrt{t_d}}\right)\) and slope is -(1 - \(\alpha\)) \(nF/RT\). In this way \(\lambda\) and \(\alpha\) can be determined. The value of \(\zeta\) can be obtained by

\[
\zeta' = \lambda D^{1/2} \quad (6.5)
\]

(b) Koutecky’s method\textsuperscript{45,46}:

If the value of standard rate constant is smaller than 3x10\(^{-5}\) then the process is totally irreversible. Then values of \(\alpha n\) and \(K_{t,h}\) can be obtained using the following equation:

\[
E = E_{1/2} + \frac{RT}{\alpha n F} \log \frac{i_d - i}{i} \quad (6.6)
\]

\[
E_{1/2} = - 0.2412 + \frac{0.0591}{\alpha n} \log \left[ \frac{1.349 K_{t,h} t^{1/2}}{D_{0}^{1/2}} \right] \quad (6.7)
\]
References


