CHAPTER II

Section (i) - Principles of Polarography
Joroslov Heyrovsky of Charles University, Prague, Czechoslovakia, first introduced polarographic technique in 1922. For his invention he was awarded Nobel prize in 1959. Polarography is an electrochemical technique which is based on the measurement and interpretation of the relationship between current and voltage during the electrolysis of unstirred solution containing electro-reducible (ions, or molecules capable of getting reduced at the cathode), or electro-oxidizable (ions, or molecules capable of getting oxidized at the anode) species. The cathode consists of drops of mercury flowing at a steady rate from a capillary tube (dropping mercury electrode), and the anode is a non-polarizable electrode such as a large pool of mercury or saturated calomel electrode. From the resulting current-voltage curves, called polarograms, it is possible to determine both the nature and concentration of the species undergoing electrode reactions.

The height of the curve is called the limiting current. This limiting current obtained with the dropping electrode is caused by a state of concentration polarization which results from the depletion of the concentration of the electrolysed substance at the electrode surface by the electrode reaction (oxidation or reduction). The current
approaches the limiting plateau when the reducible or oxidizable substance is reduced or oxidized as soon as it reaches the electrode surface and its concentration at the electrode surface remains constant at a value that is negligibly small compared to that in the body of the solution. Under these conditions, the current resulting from the electrode reaction is independent, within certain limits of the applied e.m.f. and is governed solely by the rate of supply of the reducible or oxidizable ion to the electrode surface from the surrounding solution.

In general two forces are operating when ions are supplied to the depleted region at the electrode surface. (1) a diffusive force proportional to the concentration gradient at the electrode surface and (2) an electrical force proportional to the potential difference between the electrode surface and the solution. The limiting current can, therefore, be regarded as the sum of diffusion current and the migration current.

The current through an electrolyte solution is carried by all the ions present irrespective of whether they take part in the electrode reactions or not. The fraction of the total current carried by an ion depends mostly upon its relative concentration and to a lesser degree on its charge or in other words on the transference
number of the ion. If a salt whose ions do not take part in the electrode reaction is added in excess to a solution of relatively small concentration of the reducible or oxidizable ions, the current through the solution is then transferred practically by the large excess of the added ions. Under these conditions the electrical forces on the ions taking part in the electrode reaction are practically eliminated and the limiting current becomes singularly a diffusion current.

In the case of reducible or oxidizable uncharged substances diffusion usually plays the main role in governing the limiting current because uncharged substances are not subjected to electrical migration. The indifferent salt which is added for suppressing the migration component is called the supporting electrolyte, base electrolyte, background electrolyte or carrier electrolyte. Few salts have the complexing ability too. Some metals yield waves only in certain supporting electrolytes. These salts also give a small residual current at d.m.e. which is a sum of condenser current and the faradic current due to reducible impurities present in the solution. The magnitude of the condenser current in air-free solutions with a normal capillary and drop time is a few tenths of a micro ampere. In accurate diffusion current measurements it is essential to determine the residual current in the particular supporting electrolyte used.
The diffusion current is dependent on a number of factors including the diffusion coefficient of the depolarising substance and its concentration in the body of the solution, the number of Faradays consumed in one mole of the electrode reaction and the area of the electrode. Polarographic measurements are mostly used to determine the concentration of the ion or the molecules in question but they are also valuable in studies of diffusion coefficients and the products of the electrode reaction.

An important mathematical relationship pertaining to the diffusion current is shown in the Ilkovic equation:

\[ i_d = 607 n C D^{1/2} m^{2/3} t^{1/6} \]

where
- \( i_d \) = average diffusion current, \( \mu A \ (10^{-6} \ am) \)
- \( n \) = number of Faradays per mole involved in the electrode reaction
- \( C \) = concentration of the electroactive material, millimoles/litre
- \( D \) = diffusion coefficient of the electroactive material, \( cm^2/Sec \)
- \( m \) = rate of flow of mercury through the capillary, \( mg/Sec \)
- \( t \) = time between successive drops of mercury, \( Sec \)
The terms $m^{2/3}$ and $t^{1/6}$ are dependent on the character and size of the capillary, the terms $n$, $C$, and $D^{1/2}$ are determined by the properties of the solute and solution.

Sometimes the factors pertaining to any one electrode process under a fixed set of experimental conditions are combined in a single factor $I$, called the diffusion current constant given as

$$I = 607\sqrt{nD} = \frac{I_d}{C m^{2/3} t^{1/6}}$$

The diffusion current is dependent on number of factors including the diffusion coefficient of the depolarising substance and its concentration in the body of the solution, number of faradays consumed in one mole of the electrode reaction, the area of the electrode and the transfer coefficient.

The Ilkovic equation is valid only if the wave obtained is solely due to diffusion of ions from the body of the solution to the electrode surface. This equation fails if the wave obtained is partly or wholly controlled by the kinetics of the reaction, the presence of catalytically active substances in solution or the adsorption or either the oxidised or reduced ion or groups on the surface of mercury drop. So the validity of this equation is decided
by considering whether the polarographic wave obtained, is diffusion controlled or not. To decide this the following factors are considered.

(1) $i_d$ is proportional to $m^{2/3} t^{1/6}$, when the other factors in the Ilkovic equation are constant. The drop time $t$ depends upon the heights of mercury column. Hence, if the wave is diffusion controlled $K = i_d / \sqrt{h_{\text{Hg}}}$. This is the frequently used method of ascertaining whether the height of the wave is diffusion controlled or not. If $'K'$ is not constant within the limits of experimental error over a wide range of the mercury heights it may be concluded that the current must be either partly or wholly governed by the rate of some process other than the diffusion of metal ions.

(2) 'D', is the diffusion coefficient in the Ilkovic equation is given by the Nernst equation as

$$D = \frac{R}{Z} \frac{T}{F^2} \lambda^\infty$$

where

$R$ = the gas constant in volt-coulombs per degree

$T$ = absolute temperature

$\lambda^\infty$ = the equivalent conductivity at infinite dilution

$Z$ = the charge of the ion

$F$ = the number of coulombs per Faraday
The conductivity of the solution varies rapidly with temperature causing changes in $D$ and hence in value $i^d$. Normally $D$ and $i^d$ values increase by 2 and 3 per cent respectively per degree rise in temperature. High deviations from these values are common tests for kinetic and catalytic currents.

(3) When other factors in the Ilkovic equation remain constant the diffusion current $i_d$ is directly proportional to the concentration of the reducible or oxidizable substances. Hence a graph plotted between the diffusion current and concentration of the substance should give a straight line if the wave is diffusion controlled. This forms the quantitative aspect of polarography.

Complexation of a metal ion decreases the diffusion current if the ligand is bigger in size to the water molecules it replaces and shifts the half-wave potential generally to the more cathodic value. These two variables induced by increasing concentration of ligand allow the determination of coordination number, size and stability constants of complexes in solution or serve to elucidate the kinetics of the rate determining step depending upon the type of the electrode reactions.
Maxima and Maximum suppressors

Polarographic analysis is carried out with an experimental set up that ensures drop formation undisturbed by vibration or stirring. This keeps convection in a solution at minimum. However, a convection or streaming of solution results from the electrode reaction itself and is therefore very reproducible. This phenomenon exists in a thin layer around the mercury drop. Since much more material is brought to the electrode by convection than by diffusion, the currents become very much larger than pure diffusion currents. They are easily recognisable since they are not maintained over a large voltage span but diminish more or less abruptly to the smaller value of the diffusion currents, giving rise to sharp or rounded maximum on the polarographic curves. Maxima are observed most frequently at the beginning and occasionally in the middle of the straight portion of a limiting current. A maximum may be found during a reduction or oxidation of ionised or non-ionised, organic or inorganic substances. The maxima may be acute or rounded depending on the nature and concentration of the material reduced but also on the concentration of the indifferent electrolyte and the resistance of the circuit. In general the maxima become smaller the longer the drop time of the electrode, increases with an increasing concentration of the electroactive material.
Two kinds of maxima may be observed and these are maxima of the first kind and maxima of the second kind.

Maxima of both kinds are obstacle to quantitative polarographic analyses. They can be eliminated by the addition of small quantity of maximum suppressor to the solution. This substance is adsorbed on to the surface of a dropping electrode and then retards or prevents motion of the solution past the drop surface. Most popular maximum suppressors are some of the surface active reagents like gelatin, agar, organic dyes and Triton X-100. They must be present in smaller concentration. At higher concentration they render, interpretation of polarograms difficult by diminishing the limiting current of the substance itself. The effectiveness of a suppressor can be expressed as the maximum dilution or the minimum necessary for complete suppression of a given maximum.

**Kinetic Currents**

If the rate of the chemical reaction partly or completely governs the height of the polarographic wave (limiting current), it is referred to as a 'kinetic wave'. These types of the waves follow the general mechanism as mentioned below.

\[
\begin{align*}
Y & \xrightarrow{K_f} \mathbf{0} \\
\frac{K_f}{K_r} & \\
\mathbf{0} + ne & \xrightarrow{R}
\end{align*}
\]
In the above equations '0' is reducible at potentials where 'Y' is not. But in some systems it is possible to reduce 'Y' directly at a more negative potential than is needed to reduce '0'. \( K_f \) and \( K_r \) are the psuedo first order rate constants for the forward and reverse reaction.

The mathematical expression relating the kinetic limiting current with concentration of the depolarizer is given as

\[
\eta_k = 493 \frac{n}{D^{1/2}} C_y m^{2/3} t^{2/3} \left( K_f / K_r^{1/2} \right)
\]

where

\( \eta_k \) = average kinetic current during the life of the drop
\( D \) = diffusion coefficient of \( Y \) or \( O \)
\( C_y \) = concentration of \( Y \) in millimoles per litre
\( n \) = number of electrons transferred
\( m \) = mass of the drop in milligram
\( t \) = drop time in seconds.

**Catalytic Current**

The polarographic wave corresponding to the electrode process which follows the mechanism mentioned below is referred to as 'catalytic wave'.

where 'Z' is not reduced when present alone at the electrode in the potential range of study. However, it is reduced by the reduction product 'R' to regenerate the electroactive substance 'O'. Thus the second step takes place a number of times during the life of the drop and is responsible for the great increase in the limiting current. The average catalytic current during the life of a drop is represented by the equation

\[ i_c = 493 n D^{1/2} C_0 m^{2/3} t^{2/3} \left[ (K_f + K_r)C_O Z \right]^{1/2} \]

where \( C_0 \) is the concentration of 'O' expressed in millimoles per litre.

An equation relating the rate constant and limiting current can be given as

\[ i_c = 1/5 \left( 1.255 \times 10^5 n m^{2/3} t^{2/3} D^{1/2} C_0 C_O^{1/2} k^{1/2} \right) \]

where

- \( i_c \) = average catalytic current
- \( n \) = number of electrons
- \( D \) = polarographic diffusion coefficient of the depolarizer 'O'
- \( C_0 \) = concentration of the electroactive species in millimoles per litre
C_\textsubscript{z} = \text{concentration of the electro-inactive species (z)}\text{ in the given potential range expressed in millimoles per litre}

K = \text{rate constant of the reaction producing the electroactive species.}

Application of Polarography

Polarographic analyses can be used directly for the determination of any substance solid, liquid, or gaseous, organic or inorganic, ionic or molecular that can be reduced or oxidised at dropping mercury electrode. One of the most important advantages of polarography is the determination of two or more substances by obtaining a single current-potential curve. Another important technique is the amperometric titration which involves polarographic measurements. In addition to analytical uses, polarography is one of the most fruitful techniques of research in physical, inorganic and organic chemistry. This technique is spreading more widely in subsidiary fields like biochemistry, pharmaceutical chemistry, environmental chemistry and others. It is being used to study diverse topics as hydrolysis, solubility, complex formation, adsorption, the stoichiometry and kinetics of chemical reactions, the mechanisms of electrode reaction and of chemical reactions accompanying them, standard and formal potentials, molecular dimensions, the effects of structure on reactivity, and many others of interest and importance.
Reversible and irreversible processes

Electrode reactions at d.m.e. can be broadly divided into reversible and irreversible processes. Reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. On the other hand irreversible reactions are so slow that they proceed only a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between the current and potential. Between these two electrode reactions there is an intermediate class of reactions that are fast enough to approach the equilibrium during the drop life but not quite so fast that they appear to reach it within the experimental error of the measurements. This type of electrode reactions are known as quasi-reversible reactions. The values of standard rate constant, $K_s$ of these three types of reactions are given as follows:

1. Reversible processes where $K_s > 2 \times 10^{-2} \text{ cm Sec}^{-1}$
2. Irreversible process $K_s < 10^{-5} \text{ cm Sec}^{-1}$
3. Quasi-reversible process $K_s = 2 \times 10^{-2}$ to $10^{-5} \text{ cm Sec}^{-1}$

The theory of reversible processes was well-established in the early stages of the development of the field.
Reversible electrode reactions at d.m.e.

Consider a reduction reaction occurring at the dropping mercury electrode which may be represented as

\[ O + ne \rightarrow R \quad \cdots \quad (1) \]

When the oxidised species is brought to the electrode surface it can be reduced at a proper potential. The transfer of the species is due to the three modes of transfer viz., migration, convection and diffusion. Diffusion becomes the sole mode of transfer, convection and migration being avoided. The current depends upon the kinetics of the electrochemical reaction and on the rate of mass transfer to the electrode surface. When this reaction is rapid and chemical equilibrium is attained at the electrode, the process becomes reversible, and Nernst equation can be applied. Then the potential of the electrode is given as

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_R^0}{a_O^0} \quad \cdots \quad (2) \]

where \( E^0 \) is the standard potential, \( a_R^0 \) and \( a_O^0 \) are the activities of the species at the electrode surface correlating \( E \), \( E_{1/2} \), the half-wave potential, \( i \), the current at potential \( E \) and \( i_d \) the diffusion current. Heyrovsky and Ilkovic derived the equation as
\[ E_{1/2} = E^0 - \frac{RT}{nF} \ln \left( \frac{D_o}{D_R} \right) \]  \hspace{1cm} \ldots (3)

and

\[ E_{dme} = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \]  \hspace{1cm} \ldots (4)

\[ = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \]  \hspace{1cm} \ldots (5)

where

- \( E_{dme} \) = applied potential of the dropping mercury electrode
- \( E_{1/2} \) = half-wave potential of the depolariser
- \( i \) = mean current at the applied potential
- \( i_d \) = the diffusion current
- \( n \) = number of electrons involved in the process
- \( F \) = Faraday

The above equation indicates that a plot of \( \log \frac{i}{i_d - i} \) vs \( E \) should give a straight line with slope equal to \( 0.0591/n \) volts which is the most common criteria for the thermodynamic reversibility. The intercept on the X-axis gives the half-wave potential, \( E_{1/2} \). Eventhough this linear relationship is usually taken as an important criterian for establishing reversibility of the polaro-graphic process it should be used with great caution. Very often a linear plot is obtained for processes classified as irreversible. However, in such a process the value of \( n \) is non-integer. Sometimes the observed slope of such
plot for a reversible wave may differ from theoretical value by 3-5 mV but any difference is greater than this is a proof for irreversibility. The diffusion coefficients of the oxidised $D_0$ and reduced species $D_R$ are very nearly same in number of cases. Therefore, it follows from equation (3) that the half-wave potential in the case of reversible processes is identical with the standard potential of the system.

The other factors which can be considered to decide the reversibility of an electrode process are given below. Tomes method requires the measurement of $E_{3/4}$ and $E_{1/4}$ i.e. the potentials at which the current is equal to three-fourths and one-fourths of the diffusion current. At $E_{1/4}$, we have

$$E_{1/4} = E_{1/2} - \frac{0.0591}{n} \log \frac{i_d}{i_d^{1/4}} ... (6)$$

$$E_{1/2} = E_{1/2} - \frac{0.0591}{n} \log 1/3 ... (7)$$

and at $E_{3/4} = E_{1/2} - \frac{0.0591}{n} \log 3 ... (8)$

so that

$$E_{3/4} - E_{1/4} = - \frac{0.0591}{n} \log 9 ... (9)$$

$$= - \frac{0.0594}{n} ... (10)$$
Hence for a reversible electrode reaction

\[ E_{3/4} - E_{1/4} \text{ must be equal to } -0.0564/n. \]

The half-wave potential of a reversible wave is independent of the concentration of the substance being reduced or oxidized. An appreciable variation of \( E_{1/2} \) with concentration is a proof of irreversibility of the reaction. The reverse is not true, however, for the half-wave potential of many irreversible waves are also independent of concentration.

The most conclusive proof of reversibility of a reaction is secured when polarograms of solutions containing the reduced form of redox couple involved in the reaction are found to give anodic waves whose half-wave potentials are identical with the cathodic half-wave potentials of the oxidized form. This is the same thing as securing a composite wave with no inflection around the residual current curve with a solution containing both the oxidized and the reduced forms. It is worthwhile to make sure that the cathodic and anodic 'id's obtained with equal concentrations of the reduced and oxidized species are approximately equal. In such a case the point of inflection is the redox potential of the system.

In addition to these common criteria of reversibility there are several others that are less often used, partly because special information must be obtained to permit their
The temperature coefficients of a reversible wave depends on the nature of the electrode reaction. For a reduction to a metal soluble in mercury \( \frac{dE_{1/2}}{dt} \) is about \(-0.7\) mV/degree and for a homogeneous reduction \( \frac{dE_{1/2}}{dt} \) may be either positive or negative but is rarely greater than \(+1\) mV/degree. The temperature coefficients of \( E_{1/2} \) for an irreversible wave is almost always positive and is usually of the order of several mV/degree. Larger temperature coefficients of \( E_{1/2} \) for constitute a fair evidence against the reversibility of the wave.
CHAPTER II

Sections (ii) and (iii) - Polarographic studies of cadmium and lead
Survey of literature revealed that both cadmium and lead usually have undergone reversible electrode reduction at d.m.e. with two electron reduction in the presence of complexing agents. It is also observed from the literature survey that the polarographic work on metal Schiff base complexes is not extensive. The reason may be due to the interference of \( >C=N \) in the reduction of some of the metal ions whose reduction potentials are more than that of \( >C=N \) itself. However, both cadmium and lead reduced well in advance than the \( >C=N \) reduction potential. Hence, the author has carried out polarographic studies of cadmium and lead in detail in the presence of newly synthesised Schiff base namely para-chloro acetophenone – Tris [Cl-APT].

**EXPERIMENTAL**

**Materials and Solutions**

Metal ion solutions were prepared from AR grade samples and analysed by standard methods. Potassium nitrate (0.1 M) was used to keep the ionic strength constant. Recrystallised compound was used for the preparation of the ligand solution.
The ligand solution was prepared in distilled water. Double distilled mercury was used for d.m.e. 0.002% Triton-X-100 was employed during the studies as maximum suppressor. 4% Mannitol was maintained in the studies of lead in order to suppress hydrolysis.

**Apparatus**

Current-voltage measurements were made with a CL-25 ELICO DC Recording Polarograph. The potential was applied between dropping mercury electrode and saturated calomel electrode. ELICO Glass capillary was used for d.m.e. The capillary characteristics determined in conductivity water in open circuit at constant height of mercury head (67 cm) were found to be $t = 3.8 \text{ Sec.}$ and $m = 2.480 \text{ mg Sec}^{-1}$. pH measurements were made using a ELICO pH meter. Lingane and Latimer's H-type cell was used for carrying out experiments. Dissolved oxygen was removed by passing pure hydrogen through the test solution prior to recording. The studies were carried out at 28°C.
Section (ii) - Polarographic Studies of Cadmium in presence of p-chloro acetophenone - Tris

Usually cadmium ion undergoes reversible electrode reaction in aqueous solutions as well as in presence of complexing agents. Various authors\textsuperscript{2-4, 6-9, 12,13} studied the complexing ability of cadmium in presence of Schiff bases derived from Tris (hydroxy methyl) amino methane as a common base and carbonyl compounds. In the present investigation the author employed 4-chloro acetophenone - Tris as the complexing agent, to study the polarographic behaviour of cadmium towards it. The studies include effect of hydrogen ion concentration, ligand concentration, height of mercury column and metal ion concentration on the polarographic wave of the complex.

1. Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the polarographic reduction of cadmium in presence of the complexing agent has been carried out in order to achieve an optimum pH at which a well defined reversible wave will be observed thereby enabling to perform other studies like the quantitative estimations.

The effect of pH over the polarographic reduction of cadmium in the presence of the new ligand namely 4-chloro
acetophenone - Tris as complexing agent was studied in detail. Well defined polarograms (Fig. 2) were obtained for cadmium in the pH range 3 to 11. From the results it was observed that the pH has considerable influence on the characteristics of the polarograms. Diffusion current decreased with increasing pH whereas half-wave potential shifted towards more cathodic values. The slope values calculated from \( E_{3/4} - E_{1/4} \) values (Table 2) suggested that the electrode reaction at d.m.e. was a two electron reversible reduction. pH 8.5 was fixed for other studies, such as the effect of ligand concentration, effect of height of mercury column and the effect of metal ion concentration.

2. **Effect of ligand concentration**

Usually the effect of ligand concentration on the polarographic behaviour of metal ion in presence of complexing agents will be studied to fix an optimum ligand concentration in order to get well defined polarogram thereby enabling to carry out other investigations.

Cadmium gave well defined polarographic waves (Fig. 3) in presence of 4-chloro acetophenone - Tris as complexing agent over a wide range of concentrations of the ligand (0.005 to 0.150 M). The results revealed that the diffusion
current decreased and half-wave potentials shifted towards more negative value with increasing concentration of the ligand. This observation clearly suggested that cadmium formed complexes with 4-chloro acetophenone - Tris. The slope values (Table 3) obtained from the plots of log $i/(i_d - i)$ Vs $E_{de}$ plots (Fig. 4) revealed that the polarographic reduction was two electron reduction. The graph drawn between $-\log [C]$ and $E_{1/2}$ was not a straight line but a smooth curve suggesting the existence of more than one complex species which were in equilibrium with each other.

3. **Effect of height of mercury column**

In order to ascertain the applicability of Ilkovic equation and to establish the diffusion controlled nature of the waves, the effect of mercury column height on the polarographic wave height is studied. A linear relationship between the diffusion current and the square root of the height of the mercury column suggests that the polarographic process is diffusion controlled.

Keeping the above facts in view, the author has carried out the effect of height of mercury column on cadmium wave in presence of complexing agent. The results revealed that a linear relationship exists between the
diffusion current and the square root of mercury column height, $i_d/\sqrt{h}$ values (Table 4) calculated were constant indicating the diffusion controlled nature of the wave.

4. **Effect of metal ion concentration**

To establish the usefulness of the polarogram for the quantitative determination of a particular metal ion in presence of one or more other metal ions, the effect of metal ion concentration on the wave height will be studied. The quantitative estimation will be possible only if the wave height is linearly proportional to the concentration of the metal ion present in the solution.

The effect of the metal ion concentration on the wave height has, therefore, been carried out for cadmium in presence of 0.05 M ligand (Cl - APT) and 0.1 M KNO$_3$ at pH 8.5 (Fig. 5). From the studies it was observed that the diffusion current varied linearly with the concentration of the metal ion. A calibration plot (Fig. 6) was constructed between metal ion concentration and diffusion reaction. $i_d/C$ values (Table 5) were constant within the experimental error.
**TABLE 2**

Effect of pH on cadmium - (Cl-APT) complex

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>pH</th>
<th>$i_d$ (µA)</th>
<th>$E_{1/2}$ (-V vs SCE)</th>
<th>$E_{3/4} - E_{1/4}$ (mV)</th>
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<td>3</td>
<td>5.83</td>
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</tr>
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<td>4</td>
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</tr>
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<td>11</td>
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Fig. 2. Polarograms of 1.0 mM cadmium in 0.1 M KNO₃ and 0.05 M ligand at pH (a) 3; (b) 4; (c) 5; (d) 6; (e) 8; (f) 9; (g) 10; (h) 11.
TABLE 3

Effect of ligand concentration on cadmium

Concn. of Cd$^{2+}$ ion = 1.0 mM
pH = 8.5
\([\text{KNO}_3]\) = 0.1 M
Triton-X-100 = 0.02%  

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>[Ligand] (M)</th>
<th>$E_{1/2}$ (-V vs SCE)</th>
<th>$i_d$ (µA)</th>
<th>Slope (mV)</th>
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</tr>
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<td>0.7410</td>
<td>4.86</td>
<td>28.0</td>
</tr>
</tbody>
</table>
Fig. 3. Polarograms of 1.0 mM cadmium in (a) 0.005, (b) 0.008, (c) 0.01, (d) 0.02, (e) 0.03, (f) 0.04, (g) 0.05, (h) 0.06, (i) 0.08, (j) 0.10, (k) 0.125, (l) 0.150 M (Cl - APT) and 0.1 M KNO₃ at pH 8.5.
Fig. 4. Typical log plot of 1.2 mM cadmium in 0.05 M (Cl-APT) and 0.1 M KNO₃ at pH 8.5.
TABLE 4

Effect of height of mercury column on cadmium polarograms

Concn. of Cd$^{2+}$ ion $= 1.0$ mM
Concn. of ligand $= 0.05$ M
pH $= 8.5$
$[\text{KNO}_3]$ $= 0.1$ M
Triton-X-100 $= 0.002$

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Height of the mercury column (h) (cm)</th>
<th>$i_d$ (µA)</th>
<th>$i_d/\sqrt{h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67</td>
<td>5.10</td>
<td>0.6230</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>4.80</td>
<td>0.6196</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>4.59</td>
<td>0.6189</td>
</tr>
<tr>
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<td>50</td>
<td>4.38</td>
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</tr>
<tr>
<td>5</td>
<td>45</td>
<td>4.17</td>
<td>0.6216</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>3.93</td>
<td>0.6213</td>
</tr>
</tbody>
</table>
TABLE 5

Effect of cadmium ion concentration on the wave height

Concn. of ligand = 0.05 M
pH = 8.5
\([\text{KNO}_3]\) = 0.1 M
Trition-X-100 = 0.002%

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Concentration of Cadmium ion (mM)</th>
<th>(i_d) (μA)</th>
<th>(i_d / C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40</td>
<td>2.04</td>
<td>5.100</td>
</tr>
<tr>
<td>2</td>
<td>0.60</td>
<td>3.06</td>
<td>5.100</td>
</tr>
<tr>
<td>3</td>
<td>0.70</td>
<td>3.54</td>
<td>5.057</td>
</tr>
<tr>
<td>4</td>
<td>0.80</td>
<td>4.08</td>
<td>5.100</td>
</tr>
<tr>
<td>5</td>
<td>1.20</td>
<td>6.12</td>
<td>5.100</td>
</tr>
</tbody>
</table>
Fig. 5. Polarograms of (a) 0.40, (b) 0.60, (c) 0.70, (d) 0.80, (e) 1.2 mM cadmium in 0.05 M Cl⁻ (Cl⁻ APT) and 0.1 M KNO₃ at pH 8.5.
Fig. 6. Calibration plot of cadmium in 0.05 M (Cl - APT) and 0.1 M KNO₃ at pH $\approx 8.5$
Section (iii) - Polarographic behaviour of Lead in p-chloro acetophenone - Tris as Complexing Agent

Perusal of literature reveals that like cadmium lead also undergoes reversible electrode reactions at d.m.e. usually with two electron reduction. Literature survey also suggested that not much work has been done on the polarographic reduction of lead - Schiff base complexes. Very few references are available on lead in presence of Schiff bases derived from Tris (hydroxy methyl) amino methane and carbonyl compounds. In the present study the author is, therefore, devoted his work to study complexing ability of the ligand under consideration towards lead. In order to ascertain the polarographic behaviour of lead, various studies like effect of hydrogen ion concentration, effect of ligand concentration, effect of height of mercury column and effect of metal ion concentration have been carried out.

1. **Effect of hydrogen ion concentration**

The effect of hydrogen ion concentration on the polarographic wave will be studied in order to arrive at an optimum pH at which well defined reversible waves will be obtained.

The influence of pH on the polarographic reduction of lead in presence of p-chloro acetophenone - Tris as
complexing agent and 0.1 M KNO₃ as supporting electrolyte were carried out. Well defined polarographic waves (Fig. 7) were obtained for lead from pH 3.0 to 11.0. As the pH was increased, diffusion current decreased whereas half-wave potential shifted towards more negative value indicating that the hydrogen ion concentration had considerable effect on the polarographic wave. $E_{3/4} - E_{1/4}$ values (Table 6) revealed that the electrode reaction was reversible with two electron reduction. 4% mannitol was used to suppress the hydrolysis of lead. pH 8.5 was fixed to carry out other studies like effect of ligand concentration, effect of height of mercury column and effect of metal ion concentration.

2. **Effect of ligand concentration**

In order to fix the minimum ligand concentration at which well defined and reversible waves will be obtained, the effect of ligand concentration is studied. The study also helps to carry out quantitative determination of metal ions in presence of complexing agent.

In presence of 4-chloro acetophenone – Tris as complexing agent lead gave well defined polarograms (Fig. 8), over the entire range of concentration of the ligand studied (0.005 to 0.150 M). Hence, 0.05 M concentration of the ligand was fixed to carry out for other studies.
The data obtained for this study suggested that the diffusion current decreased and half-wave potentials shifted towards more cathodic value with increasing concentration of the complexing agent. This clearly showed that 4-chloro acetophenone - Tris behaved as good complexing agent towards lead. The slope values (Table 7) determined from the log plots (Fig. 9) for different concentrations of ligand revealed that the reduction was reversible involving two electron reduction. The graph constructed between $-\log [C]$ and $E_{1/2}$ gave a straight line indicating the existence of only one stable complex species.

3. **Effect of height of mercury column**

To establish the applicability of Ilkovic equation and to ascertain the diffusion controlled nature of the polarographic wave, the effect of height of mercury column on the polarographic reduction wave will be studied.

The influence of mercury column height on the polarograms was carried out for lead in presence of the ligand and 0.1 M KNO$_3$ at pH 8.5. The results showed that $i_d/\sqrt{h}$ values (Table 8) were constant within the experimental error, indicating the diffusion controlled nature of the wave. The graph drawn between diffusion current and square root of height of mercury column gave a straight line passing through the origin.
4. **Effect of metal ion concentration**

In order to verify the validity of Ilkovic equation and thereby extending it to quantitative estimation of metal ions either single or in combination, the effect of metal ion concentration on the wave height will be studied. This is possibly only when the wave height varies linearly with metal ion concentration present in solution.

The study of effect of metal ion concentration on the polarographic wave was carried out in presence of 0.05 M complexing agent and 0.1 M KNO$_3$ as supporting electrolyte at pH 8.5 (Fig. 10). From the results it was quite evident that the diffusion current varied linearly with concentration of the metal ion. A calibration plot drawn (Fig. 11) for metal ion concentration and diffusion current gave a straight line passing through the origin. $i_d / C$ values (Table 9) calculated were constant within the experimental error.
TABLE 6

Effect of pH on lead - (Cl-APT) complex

Concn. of Pb$^{2+}$ ion = 1.0 mM
Concn. of ligand = 0.05 M
$[\text{KNO}_3]$ = 0.1 M
Triton-X-100 = 0.002%

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>pH</th>
<th>$i_d$ (μA)</th>
<th>$E_{1/2}$ (-V vs SCE)</th>
<th>$E_{3/4} - E_{1/4}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>7.20</td>
<td>0.4900</td>
<td>0.027</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>4.85</td>
<td>0.4980</td>
<td>0.027</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>4.60</td>
<td>0.5055</td>
<td>0.028</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4.34</td>
<td>0.5135</td>
<td>0.029</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>3.84</td>
<td>0.5215</td>
<td>0.030</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>3.66</td>
<td>0.5290</td>
<td>0.030</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>3.34</td>
<td>0.5450</td>
<td>0.030</td>
</tr>
<tr>
<td>8</td>
<td>11</td>
<td>3.28</td>
<td>0.5525</td>
<td>0.030</td>
</tr>
</tbody>
</table>
Fig. 7. Polarograms of 1.0 mM lead in 0.1 M KNO₃ and 0.05 M (Cl - APT) at pH (a) 3, (b) 4, (c) 5, (d) 6, (e) 8, (f) 9, (g) 10, (h) 11.
TABLE 7

Effect of ligand concentration on lead

Concn. of Pb\(^{2+}\) ion = 1.0 mM

pH = 8.5

\([\text{KNO}_3]\) = 0.1 M

Triton-X-100 = 0.002%

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>[Ligand] (M)</th>
<th>(E_{1/2}) (V vs SCE)</th>
<th>(i_d) (µA)</th>
<th>Slope (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.4000</td>
<td>4.44</td>
<td>29.00</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.4825</td>
<td>4.14</td>
<td>32.20</td>
</tr>
<tr>
<td>3</td>
<td>0.008</td>
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<td>32.18</td>
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<tr>
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<td>0.010</td>
<td>0.4940</td>
<td>4.06</td>
<td>32.00</td>
</tr>
<tr>
<td>5</td>
<td>0.020</td>
<td>0.5050</td>
<td>3.96</td>
<td>32.00</td>
</tr>
<tr>
<td>6</td>
<td>0.030</td>
<td>0.5150</td>
<td>3.90</td>
<td>31.68</td>
</tr>
<tr>
<td>7</td>
<td>0.040</td>
<td>0.5200</td>
<td>3.84</td>
<td>30.00</td>
</tr>
<tr>
<td>8</td>
<td>0.050</td>
<td>0.5250</td>
<td>3.75</td>
<td>29.50</td>
</tr>
<tr>
<td>9</td>
<td>0.060</td>
<td>0.5275</td>
<td>3.66</td>
<td>29.50</td>
</tr>
<tr>
<td>10</td>
<td>0.080</td>
<td>0.5350</td>
<td>3.48</td>
<td>29.40</td>
</tr>
<tr>
<td>11</td>
<td>0.100</td>
<td>0.5425</td>
<td>3.42</td>
<td>29.40</td>
</tr>
</tbody>
</table>
Fig. 8. Polarograms of 1.0 mM lead in (a) 0.005, (b) 0.008, (c) 0.01, (d) 0.02, (e) 0.03, (f) 0.04 (g) 0.05, (h) 0.06, (i) 0.08, (j) 0.10 M (Cl - APT) and 0.1 M KNO₃ at pH 8.5.
Fig. 9. Typical log plot of 1.4 mM lead in 0.05 M (Cl – APT) and 0.1 M KNO₃ at pH = 8.5.
TABLE 8

Effect of height of mercury column on lead polarograms

Concn. of Pb$^{2+}$ = 1.0 mM
Concn. of ligand = 0.05 M
pH = 8.5
[KNO$_3$] = 0.1 M
Triton-X-100 = 0.002%

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Height of the mercury column (h) (cm)</th>
<th>$i_d$ (µA)</th>
<th>$i_d \sqrt{h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67</td>
<td>3.75</td>
<td>0.4581</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>3.54</td>
<td>0.4570</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>3.42</td>
<td>0.4611</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>3.24</td>
<td>0.4582</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>3.06</td>
<td>0.4561</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>2.94</td>
<td>0.4648</td>
</tr>
</tbody>
</table>
### TABLE 9

**Effect of lead ion concentration on the wave height**

Concn. of ligand = 0.05 M  
\[ \text{pH} = 8.5 \]  
\[ [\text{KNO}_3] = 0.1 \text{ M} \]  
\[ \text{Triton-X-100} = 0.002\% \]

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Concentration of lead ion (mM)</th>
<th>1_d (μA)</th>
<th>1_d / c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40</td>
<td>1.50</td>
<td>3.75</td>
</tr>
<tr>
<td>2</td>
<td>0.60</td>
<td>2.25</td>
<td>3.75</td>
</tr>
<tr>
<td>3</td>
<td>0.70</td>
<td>2.64</td>
<td>3.77</td>
</tr>
<tr>
<td>4</td>
<td>0.80</td>
<td>3.00</td>
<td>3.75</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
<td>3.75</td>
<td>3.75</td>
</tr>
<tr>
<td>6</td>
<td>1.20</td>
<td>4.50</td>
<td>3.75</td>
</tr>
<tr>
<td>7</td>
<td>1.40</td>
<td>5.25</td>
<td>3.75</td>
</tr>
</tbody>
</table>
Fig. 10. Polarograms of (a) 0.40, (b) 0.60, (c) 0.70, (d) 0.80, (e) 1.0, (f) 1.2, (g) 1.4 mM lead in 0.05 M (Cl - APT) and 0.1 M KNO₃ at pH 8.5.
Fig. 11. Calibration plot of lead in 0.05 M (Cl - APT) and 0.1 M KNO₃ at pH ≈ 8.5.
References


