CHAPTER II

METHODS AND PRINCIPLES
The study of the complex formation in solution is becoming increasingly popular in the recent years and a number of physical methods have been developed to study various stoichiometric and structural aspects of soluble complexes. Now a days isolation of the compound, followed by subsequent chemical analysis has been the procedure adopted by a large number of workers. But in most of the cases the isolation of the compound in pure form is rather difficult and hence chemical analysis may not be relied upon. That is why, the study of complex compounds in solution is restricted to the application of physico-chemical methods. Only a few of the large number of commonly applied methods may be quoted here as an illustration. The author has isolated the complexes in the pure form and i.s. studies was performed.

(1) X-ray method:

X-ray studies offer a direct proof for the existence of chelate rings and complex formation. The determination of structure of crystalline compounds by x-ray analysis has been in the detection of the co-ordinate linkages and distribution of bonds about a co-ordinate centre. The main difficulty in applying the x-ray method is in obtaining the crystalline materials in proper form for analysis and hence the applicability fo the method is restricted to a small number of substances.
(2) **Ion-exchange method:**

Ion exchange reaction have come to be a powerful weapon in the hands of chemists for the study of the solutions of electrolytes. In this method ions from a solution are exchanged (adsorbed) for other ions from exchange medium. The covalent linkage between a metal and a donor is characterized by low exchange rates with free metal ion in solution. The low exchange rate is responsible for the formation of complex or a chelate.

(3) **Colligative method:**

Colligative properties such as (i) Osmotic pressure, (ii) Lowering of freezing point and (iii) Elevation of the boiling point of solutions containing complex ions show abnormally low colligative effects and also lower conductivity than the expected one, because they contain fewer particles of solute than would otherwise be present. For example, when mercuric iodide, is added in small amount to a solution of potassium iodide, the freezing point depression is less than before, because of the formation of complex ion from simple ions, thus,

\[ 2K^+ + 2I^- + HgI_2 \rightleftharpoons 2K^+ + (HgI_4)^{-2} \]

when potassium iodide and mercuric iodide are present in molecular proportion 2:1 respectively the depression is only three quarters of its original value since there are
only three ions in solution for every four that existed before.

A few more methods have been employed by various workers, from time to time to study complex compounds. Thus (4) The velocity of Ultrasonic waves, (5) The magnetic susceptibility, (6) the dialysis, (7) Raman spectroscopy, (8) The radio active tracer technique, (9) The infra-red spectroscopy, (10) The optical rotation, (11) The Nuclear magnetic resonance, (12) The electrophoresis, (13) The electron paramagnetic resonance and (14) The electro motive force methods etc.

Methods employed for the present investigation for incorporated in this thesis, the author has taken recourse to the method of (a) Molar ratio method of Yoe and Jones(1), (b) pH-metric method for direct and ratio titration, (c) Job's(3) method of continuous variation, (d) Bjerrum's method (2), (e) Polarographic method and (f) Isolation method.

The index properties studied are pH for direct and ratio titration, optical density for Job's method of continuous variation, and molar ratio method, measurement of halfwave potential (E 1/2) for polarographic studies to determine the stoichiometry of the complex systems. Stability constants of the complexes were determined by Bjerrum's method using pH as index property, and Job's method using optical density as index property and lastly polarographic method using halfwave potential as index property.
A Molar Ratio Method:

The credit for devising this method for the investigation of the empirical formulae of the coloured complexes in solution goes to Yoe and Jones. They have assumed the reaction between the two components according to the equation: \( A + nB = AB_n \). They found that for a very stable complex a plot of optical density (absorbance) against the molar ratio of the component \( B \) to \( A \) with \( A \) constant, rose from the origin as a straight line. This line broke sharply to a constant optical density (absorbance) at a molar ratio \( A/B \) of the components in the complex if both components are colourless. In the case where the reagent solution is coloured the curve instead of being perfectly horizontal shows a gradual change in slope, the angle depending upon the degree of absorbance of the reagent solution (4). If the coloured component is taken as constant the curve becomes horizontal after the break at the molar ratio of the complex \( B/A \). However, if the complex undergoes appreciable dissociation in solution no sharp break is obtained. For such cases a modification of the molar ratio method has been suggested by Harvey and Manning (5,6) where they have taken and accounts the adjustment of ionic strength with the addition of an indifferent electrolyte. This method in general is termed as spectrophotometric titration.

The advantages of this method are as follows:
The existence of more than one compound in solution can be detected and their compositions established directly from the graphs. As the total volume of the mixed solution is kept constant, no volume correction is to be made. The method has been employed successfully by several workers viz., Meyer and Ayres (7), Nayer and Pande (8) who applied a similar method using conductance as the index property to determine the composition of the complex formed in solution. They have termed this method as monovariation method.

B - I Direct Titration Method :- (Index property pH).

Direct titrations of Neodymium perchlorate solution against ten times concentrated solution of ligands were carried out in the presence and absence of alkali, NaOH. The volume of the ligands were plotted against the pH.

B - II Ratio Titration Method :-

In this method the composition was confirmed by titrating the mixture of metal perchlorate and the ligands. The equimolar solutions of metal perchlorate and ligands are in different (1:1 ; 1:2, 1:3) ratio were mixed and kept (for some time so that complexation may be complete) to attain equilibrium. These mixed solutions were titrated with concentrated alkali. The volume of alkali was plotted against the pH.
C. Job's Method of Continuous Variation:

Remarkable contribution for the investigation of the complexes in solution was made by Job, who further confirmed that his method could be applied to a system where only one complex is formed (9). But Vosburgh and Cooper (10) modified this method for determining the formation of more than one complex in the system. Since, in this method the measured property should be additive, Job utilized the absorption of light as the index property. Purukayastha and Sen Sharma (11) made use of molar conductance.

The formation of a complex can be represented in general by the reversible reaction:

\[ mA + nB \rightleftharpoons A_mB_n \]

By the application of the law of mass action we can arrive at an equation:

\[
K_d = \frac{(m+n-1)^{(n-1)}}{C_p} \frac{(p_m+n)^{x-n}}{(m+n)^m} \frac{(m+n)^{p-1}}{(m-1)^m (n-1)^n} \frac{n-(m+n)^x}{(p-1)^{n-(m+n)}} 
\]

where \( K_d \) = dissociation constant

\( c \) = molar concentration of metal per ml.

\( m \) = number of metal ions.

\( n \) = number of ligand ions.

\( p \) = molar concentration of ligand/molar concentration of metal.
x ... concentration of ligand where the maximum amount of complex is formed.

When \( p = 1 \), the right hand side of equation (A) becomes zero and we have \((m + n)x = 0\) or \(m/n = (1-x)/x\). Thus by the use of equimolar solutions of \( m \) and \( l \), we can find out the ratio of \( m/n \) i.e. the composition of the complex, provided the value of \( x \) is known.

**Stability of co-ordination compounds**:

The most important factor in the investigation of co-ordination compounds lies in the determination of their stabilities. The effect of various factors on complex formation can be best understood from the formation constants of resulting compounds. The formation constants express quantitatively is the tendency of the complex ion to be formed from its original components.

On the basis of Arrhenius's theory of electrolytic dissociation and Werner's co-ordination theory a thorough investigation was carried out by Abegg and Bodlander (12) regarding the stability of the complexes. The equilibrium reaction yielding a complex containing the metal ion \( A \) and the ligand \( B \) can be represented by the following equation:

\[
K_s = \frac{[A_mb_n]}{[A]^m[B]^n} \quad \ldots \ldots \ (B)
\]

where \( K_s \) is known as overall stability constant of the complex
Determination of Stability of Complexes:

(1) By Job's method:

The author has determined the stability constants by an application of Job's method of continuous variation, using optical density as index property. From the knowledge of the composition of complex the value of $K_S$ can be determined from the expression (B) by substituting the values of $m$ and $n$, e.g. for a 1:1 ($A:L$) complex, $n = 1$ and $m = 1$, we get,

$$K_S = \frac{(p-1) \ (1-2x)}{C \ \left\{ (p+1) \ x-1 \right\}^2} \quad (C)$$

and for 1:2 ($A:L$) complex, where $m=1$ and $n=2$, we get,

$$K_S = \frac{(p-1)^2 \ (2-3x)}{C^2 \ p \ \left\{ (p+2) \ x-2 \right\}^3} \quad (D)$$

The value of $p$ (the ratio of concentration of ligand to the concentration of metal) should not be equal to one i.e. non-equirar mal solutions ($p \neq 1$) of ligand and metal should be used. Stability constant is the reverse of dissociation constant. Hence a stable complex will have small value of the dissociation constant.
(ii) By Bjerrum's method:

Bjerrum in a review has pointed out that the formation complex always occurs in stepwise fashion, with the stabilities of various species $MA$, $MA_2$ ..... $MA^n$ characterised by a series of mass action constants, $k_1$, $k_2$ ..... $k_n$. The general equilibrium between the central metal ion $M$ and $n$ donor molecules or ions $A$ may be considered to be (where $A$ is the conjugate base of a weak acid)

\[
\begin{align*}
K_1 & = \frac{(kA)}{(M)(A)} \\
K_2 & = \frac{(kA_2)}{(kA)(A)} \\
K_n & = \frac{MAN}{(kAn-1)(A)}
\end{align*}
\]

The complex (or chelate) formation constants could then be expressed by:

\[
\begin{align*}
K_1 & = \frac{(kA)}{(M)(A)} \\
K_2 & = \frac{(kA_2)}{(kA)(A)} \\
K_n & = \frac{MAN}{(kAn-1)(A)}
\end{align*}
\]

Where ( ) expresses activities of species in solution.
Bjerrum pointed out that the pH of a solution is directly affected by chelate formation, since mostly the chelating agents are acids or bases and formation of the chelate is accompanied by the displacement of proton from the acid or by decrease in concentration of the base. The increased activity is a result of the competitive binding tendencies of two Lewis acids, hydrogen and metal ions, for a Lewis base.

In order to simplify the physical analysis of the problem, Bjerrum has introduced several new concepts and relations, one of these is the quantity \( n \), (pronounced 'enbar'), the degree of formation of the system, which is defined as the average number of molecules of ligand bound per mole of metal. It may be expressed mathematically as;

\[
\bar{n} = \frac{\text{Total number of ligand } A \text{ bound to } M}{\text{Total number of } M \text{ present in the system.}}
\]

or

\[
\bar{n} = \frac{\text{Total concentration of ligand } A \text{ bound to } M}{\text{Total concentration of } M \text{ in the system.}}
\]

or

\[
\bar{n} = \frac{(MA) + 2(MA_2) + \cdots + n(MAn)}{(M) + (MA) + \cdots + (MAn)}
\]

Equation number (e) may be obtained in terms of (A).
(The concentration of unbound complexing agent), and various formation constants \( k_1, k_2 \ldots k_n \), by substitution of equation (5), (C), (U) into equation (e).
\[ \bar{n} = \frac{K_1 (A) + 2K_1 K_2 (A)^2 + \cdots + n K_1 K_2 \cdots K_n (A)^n}{1 + K_1 (A) + K_1 K_2 (A)^2 + \cdots + K_1 K_2 \cdots K_n (A)^n} \] 

Equation (f) is the so-called Bjerrum formation function.

If the concentration of unbound ligand \((A)\) can be determined experimentally, \(\bar{n}\) can be calculated from equation (g) given below:

\[ \bar{n} = \frac{C_A - (A)}{C_M} \]  

(g)

where \(C_A\) and \(C_M\) denote the total concentrations of ligand and metal ion respectively. Solution of equation (g) for the formation constants requires the use of \(n\) sets of \(\bar{n}\) and corresponding \((A)\) values.

Bjerrum's early determinations and calculations with unidentate ligands required the solution of as many as six simultaneous equations. Consequently he restarted to approximation techniques with led to development of the graphical determination of consecutive formation constants from a plot of \(\bar{n}\) values as a function of \(p(A)\), the negative logarithm of the free ligand concentration. The plot was called the formation curve of the system. A detailed mathematical treatment, as given by Bjerrum (13) may not be necessary and it will suffice for the purpose of this treatment to consider a first approximation which relates \((A)\) to \(K_n\) at \(\bar{n} = n - 1/2\):
\[ kn = \frac{1}{(A) n^{-1/2}} \]  

(h)

Thus it is possible to approximate \( \log K_1 \), \( \log K_2 \) and \( \log K_3 \) from \( \text{pA} \) at \( \bar{n} \) values of 0.5, 1.5 and 2.5 respectively. Application of Bjerrum's graphical techniques to the interaction of imidodiacetic acid with metal ions were made by Chaberek and Martell (14).

Several current methods for obtaining \( K_1 \) and \( K_2 \) from formation curves are given below:

(a) **Solution of simultaneous equations** :

For \( n=2 \) equation (f) becomes,

\[ \bar{n} + (\bar{n} - 1) K_1 (A) + (\bar{n} - 2) K_1 K_2 (A)^2 = 0 \]  

(i)

The required values of stability constant can be obtained by solving pairs of simultaneous equation derived from (i)

(b) **Successive approximation** :

From equation (i) we have,

\[ K_1 = \frac{1}{(A)} \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n}) K_2 A} \]  

(j)

and \[ K_2 = \frac{1}{(A)} \frac{\bar{n} + (\bar{n} - 1) K_1 A}{(2-\bar{n}) K_1 (A)} \]  

(k)

Bjerrum applied these equation to the refinement by successive approximation of "temperory constants" obtained by other methods.
(c) Bjerrum's spreading factor method:

At the mid point of the formation curve, when \( \bar{n} = 1 \), \( K_1 K_2(A)^2 = 1 \) or \( \log K_{AV} = p(A) \) and

\[
\log k = \log K_1 K_2 = 2p(A) \quad \quad \quad \quad \quad (L)
\]

The spreading factor \( x \) is related to the mid point slope \( \nu_1 \) of the formation curve at \( \bar{n} = 1 \) by the expression;

\[
\nu_1 = \frac{-2.303}{1 + x}
\]

From the measured mid point slope, the ratio \( K_1/K_2 \) may be calculated, and the individual values of \( K_1 \) and \( K_2 \) are obtained from the equation (L).

(d) Schwarzenbach's graphical method:

Schwarzenbach (15,16) has also described a graphical method for the composition of stability constants. This method is adopted to the computation of stability constants from experimental values of \( \bar{n} \) and \( (A) \) by plotting values of;

\[
x = \frac{(\bar{n} - 1)(A)}{\bar{n}} \quad \quad \quad \text{and}
\]

\[
y = \frac{(\bar{n} - 1)}{(2-\bar{n})(A)}
\]

as abscissa and ordinates respectively. All lines passing through pair of points \( (x,y) \) should intersect when extrapolated at the point \( (1/K_1, K_2) \).
Another manner of finding out stability constant is in terms of standard free energy change, \( \Delta G \) i.e. difference in free energies of the products and the reactants in a standard state, which is related to the equilibrium constant by the relation

\[
\Delta G = RT \log K
\]

where \( \Delta G \) is in cals./mols., \( R \) is the gas constant (1.99 cals./degree mole) \( T \) is the absolute temperature and \( K \) is the equilibrium constant.

In the present investigations Bjerrum - Calvin method (17) has been used for the determination of stability constants of the complex. Since 1:1 and 1:2 complexes are formed, values of \( pA \) at \( \bar{n} = 0.5 \) and 1.50 respectively are considered for stability constants.
POLAROGRAPHIC METHOD

The polarographic technique was first originated by Jaroslav Heyrovsky (18) of the Charles University, Prague in 1921, but it remained unappreciated till 1934, when Ilkovic (19) derived the equation which bears his name and is the theoretical cornerstone of quantitative polarography. Holthoff (20) is responsible for the widespread development of this technique in the United States. His studies of polarographic theory and practice, provided a sound basis for the understanding of each of the factors influencing the polarographic wave.

When an electrolyte solution is electrolysed in a cell consisting of a dropping mercury electrode and another non polarizable electrode, it is possible to determine from the resulting current voltage curve, both the nature and concentration of the electro reducible or oxidizable substance or substances present in the solution. This technique serves for the identification, detection and determination of trace constituents of which only a few micrograms may be present in as little as a few tenths of a milliliter of the solution. It is also used to determine the composition and stability of complex ions.

A substance (which is always added in excess to the solution to be polarographed) which does not take part in the electrode reaction, but plays an important role in supporting the current due to the electrical migration of ions
is termed as a supporting electrolyte or indifferent electrolyte. A variety of substances have been used as supporting electrolytes in developing polarographic method for the detection and determination of elements in the simple solution or in mixture.

If an unstirred solution of cadmium ions be electrolysed between the two electrodes, one of which is a dropping mercury electrode, then the current voltage curve will have a same shape as shown in the figure.

\[ \text{Applied potential in volts vs. S.C.E.} \]

\[ \text{Polarogram of Cd in 0.1 M succinic acid.} \]

- Limiting current \( \cdots AB \)
- Residual current \( \cdots AB \)
- Diffusion Current \( \cdots ED \).
As the applied potential is increased (i.e. the cathode is made more negative) a very small current flows in the beginning. As the applied potential exceeds the decomposition potential of the cadmium solution, the current starts increasing linearly till it reaches a steady value at \( D \) (shown in fig.). After this point, the current becomes independent of the applied potential. The current at \( D \) (given by the distance \( AD \) in figure) is called the limiting current. Since it is limited solely by the rate at which Cd ions from the body of the solution reach the electrode surface where they are reduced immediately. The cathode is said to be concentration polarized and the current flowing through the cell depends on the concentration of the Cd ions in the bulk of the solution. The limiting current \( AD \) is a sum of the three components (i) Residual current, (ii) Migration current, (iii) the diffusion current.

The residual current is the small current which would flow even in the absence of an electro oxidizable or reducible substance in the solution. The migration current is caused by electrostatic forces, they are operative between the electrodes and the solution.

The indifferent salt added to eliminate the migration component of the limiting current is called the "supporting electrolyte".

**Halfwave potential** \( E_{1/2} \) :-

It is that point on the potential axis when current is one half of the value of the diffusion current (id)
correcting first for the residual current due to impurities of changing of the double layer. \( n_{1/2} \) is roughly equivalent to the standard reduction potential of the species being reduced. It is expressed in volts with reference to the saturated calomel electrode and is generally constant and independent of concentration for any one depolarizing species in any one of the supporting electrolytes. It is, therefore, used for identifying a particular substance responsible for the wave.

The diffusion current \( id \), depends on a number of factors, namely, the concentration of depolarizing substance in solution, its diffusion coefficient, and number of Faraday's consumed in one mole of the electrode reaction, the area of the electrode. The diffusion current obtained with a dropping mercury electrode is given by Ilkovic equation. (It shows the relation of diffusion current and the concentration of the reducible ion).

\[
1/2 \quad 2/3 \quad 1/6 \quad 607 \quad n \quad c^D \quad m \quad t \quad ---- \quad at \quad 25^\circ C. \quad (I)
\]

- \( n \) ... number of electrons involved in the reaction.
- \( id \) ... average diffusion current in \( \mu \) amp.
- \( c \) ... concentration of the oxidizable or reducible or species present in solution.
- \( D \) ... diffusion coefficient of the reducible or oxidizable species.
- \( m \) ... mass of mercury in mg. flowing per second, expresses as mg. sec.\(^{-1}\)
- \( t \) ... drop time in second.
Under such conditions the diffusion current $i_d$ is directly proportional to the concentration of the depolarizer in the solution. If a graph is plotted against $i_d$ and the concentration of the depolarizer in solution, a straight line passing through the origin is obtained. This relation forms the basis of the quantitative determination by polarographic analysis.

If the reaction taking place at the dropping electrode is reversible, then the polarographic method may be applied advantageously to the study of complex metal ions. The condition for studying the nature of the complex is that of the polarographic wave should be thermodynamically reversible. The thermodynamic reversibility of an electrode reaction is decided on the basis of the following points.

(I) Considering the electrode reaction to be thermodynamically reversible, the potential at any point on the current voltage curve is given by the relation;

$$E_{d_e} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{id-i}$$

(II)

$E_{d_e}$ ... potential at any point on the current voltage curve

$E_{1/2}$ ... halfwave potential

$i$ ... current at any point on the current-voltage curve corresponding to $E_{d_e}$

$id$ ... diffusion current.
If the reaction is reversible, the plot of $E_d$ vs. log $1/(id-1)$ should give a straight line, with a slope equal to $0.0591/n$. The zero intercept of this plot gives the halfwave potential of wave and no systematic divergence of the points from the straight line may be found over a wide range of log terms from at least $-1.5$ to $+1.5$.

(II) The halfwave potential of a reversible wave is independent of the concentration of the oxidizable or reducible species.

(III) An additional criterion for reversibility is the fact that $E_{1/2}$ in the reduction of the metal ion should coincide with the halfwave potential of the anodic wave of the metal amalgam in the same medium.

**Theory in complexation:**

The halfwave potentials of a simple metal ions are shifted (generally to more negative values) when the metal ions undergo complex formation. The shift in the halfwave potential ($E_{1/2}$) is measured as a function of the concentration of the complexing agent and both the formula and the dissociation constant of the complex is thereby determined. The dissociation constant of the complex formed is calculated from the equation:

$$E_{1/2} (c) - E_{1/2} (s) = \frac{0.0591}{n} \log K_c - \frac{0.0591}{n} p \log cx \quad (III)$$
where $E_{1/2}^{(c)}$ ... half wave potential of complex ion.

$E_{1/2}^{(s)}$ ... half wave potential of simple metal ion.

$p$ ... the number of complex molecules of ligands around the central cation.

$n$ ... is the number of electrons involved in reduction.

$c_x$ ... the concentration of the complexing agent.

$K_c$ ... the dissociation constant of the complex.

The coordination number 'p' of the complex is given by the equation;

$$\frac{\Delta E_{1/2}}{\Delta \log c_x} = \frac{0.0591}{n} \times p \quad (IV)$$

where $n$ is the number of electrons taking part in the reaction, if a graph be plotted with halfwave potential vs. $\log c_x$, a straight line is obtained with a slope of $0.0591 \frac{p}{n}$. Therefore, if $n$ is known, 'p' can be find out and putting this value of $p$ in equation (IV), $K_c$ dissociation constant may also be calculated.

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