CHAPTER II

METHODS & PRINCIPLES
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In the case of a sparingly soluble or insoluble co-ordination compound the process of isolation, purification and chemical analysis may be pursued for its evaluation. But in most of the cases the isolation of the compound in pure form is rather difficult and hence the chemical analysis may in such cases lead to erroneous results. If the chelate formed exists in a mobile equilibrium its isolation may be faulty as in this process the equilibrium may be disturbed. It is also well known that the complex ion present at the solution stage may be different than that present in the solid state. In some cases the isolation of the complex ion, detected in solution, may not be possible at all. The physico-chemical methods applicable to the study of complex ions in equilibrium have, therefore, been widely applied in this field.

A. A large number of methods using variety of properties of the complex ion system for their detection and determination are available in literature. The use of these properties as the index for complex formation has been possible as there is a considerable drift from the normal behaviour of the compounds during complexation and more so during the chelate formation. Only a few of the large number of commonly applied methods may be quoted here as an illustration.
(i) Potentiometric methods:

During complex (chelate) formation there is a reduction in the ionic activity of the metal and hence such processes are accompanied by an increase in its oxidation potential. Advantage of this fact is taken and e.m.f. measurements during potentiometric titrations are used for investigations of the complex ion systems.

Application of this method was, probably, suggested by Bodlander (1) and the mathematical treatment for the method was afterwards given by Leden (2). Since then it has found a wide application in the field of co-ordination chemistry (3).

(ii) Polarographic methods:

The reduction of the metal ion at the dropping mercury electrode provides information which can be profitably used for the study of complex (chelate) in aqueous as well as non-aqueous media. Half wave potential of the solution is its characteristic, independent of its concentration. The complex ion is not reduced readily at the dropping mercury cathode and hence its half wave potential is more negative. Heyrovsky (4) used this fact to investigate the stability of complex ions and he then gave a detailed treatment of the procedure in 1941(5). This method is also quite common and a number of references are available in the literature on it (6).

(iii) Methods based on pH measurements:

The pH of the solution in many cases is directly
affected during complex (chelate) formation, because the chelating agents are acids or bases and formation of the co-ordination compound is accompanied by the displacement of a proton from the acid or by the decrease in concentration of the base. This fact was taken into consideration by Bjerrum (7). Now the Bjerrum method has been reported to be the most reliable and accurate method for the determination of stability constants of the co-ordination compounds. This method, therefore, enjoys popularity (8) in this field. The results obtained here can be used graphically or mathematically to calculate the stability constants (9).

(iv) Other methods:

A passing reference to a few more methods may be made to denote their variety. Thus 'Ion exchange method' (10), 'Radioactive tracer technique' (11), 'Infra-red spectroscopy' (12), 'Magnetic susceptibility' (13), 'Nuclear magnetic resonance' (14), 'Electron para-magnetic resonance' (15), 'Electrophoresis' (16), 'X-ray measurements' (17), 'Raman spectroscopy' (18) have been applied for the investigations of complex ions in addition to numerous other methods. The methods applied, very well illustrate the diversity of complex ion properties for their investigation.

(v) Methods for coloured systems:

The present investigation involves the study of coloured metal ligand systems. Such coloured systems are investigated by two different techniques (a) Matching of the colour of the system with that of the standard solution,
the technique being termed colorimetry. (b) By measurement of light absorption and the procedure being termed absorptiometry, where a restricted band of wavelength is used as incident light. It is more commonly known as spectrophotometry which employs monochromatic light as the incident ray. The coloured solutions obey 'Beer's law' under these conditions.

A short review of the methods applied for the investigation of such coloured systems may not be out of place. A number of methods based on absorbance as the index property have been suggested for determining the empirical formulae of the coloured complex ions and some of the methods are listed below:

1. Method of continuous variation. (19)
2. Vosburgh and Cooper method. (20)
3. Yoe and Jones' Molar ratio method. (21)
4. Molland Method. (22)
5. Bent and French Method. (23)
6. Edmond and Birnbaum Method. (24)
7. Slope ratio method of Manning and Harvey. (25)
8. Method of corresponding solutions. (26)
9. Straight Line Method. (27)

Method of continuous variation, Molar ratio method, Slope ratio method and Vosburgh and Cooper method have been more commonly applied from amongst the above referred ones. They are all spectrophotometric methods using light absorption as the index property. Method of corresponding solution is another common method according to Ernst and Mashi (28).
Bent and French method and Edmond and Birnbaum method
are logarithmic methods and are generally applied for the
study of weak complexes in highly dissociated condition.
Harvey and Manning's slope ratio method and the straight line
method of Asmus are also applied for the weak complexes in
solution. Holland's method is applicable only in some
special cases. Spectrophotometric methods have also been
applied to the study of step-wise formation of co-ordination
compounds by Bjerrum (26), Newmann and Hume (29) and
Yatsimirskii (30) etc.
B. The chelate systems under investigation here are
expected to be quite stable and hence the following methods
have been selected to study them in aqueous medium.
(i) Method of continuous variation (ii) Vosburgh and Cooper
method and (iii) Molar ratio method of Yoe and Jones. The
last named has been employed to study the empirical formulae
of the metal chelates at different pH. The method of
continuous variation has also been applied to calculate the
stability constants.

(1) Method of continuous variation:
This method is generally ascribed to Job (19) although
similar methods have been discussed prior to him by a number
of workers (31-34). The credit goes to Job as his presenta-
tion of the method is of a more general nature. Its success
with spectrophotometric measurements made it more useful.
It has also been reported that its application using other
properties as index led to ambiguous results (35).
This method involves the use of any additive molecular property as the index. Isomolar solutions of the metal and the ligand are mixed in varying proportions, the total volume of the mixture being kept constant. The difference (Y) between each value found for the mixed solution and the corresponding value of the property calculated for no reaction of the components is plotted against the composition of the mixture. The variation in the additive property is studied in terms of the composition of the complex. The resulting curve thus obtained (Y against composition) should pass through a maximum if the property measured has a large value for the complex ion than for the components or it passes through a minimum if the value is smaller. The composition of the mixture at this point can precisely be taken to be corresponding to that of the complex ion present in the system.

The mathematical treatment to the method was given by Job (19) himself in the following manner. He chose to represent the complex formation by the general equilibrium equations:

\[ m \text{M} + n \text{L} \rightleftharpoons M \text{M} \text{L}^n \ldots \] (1)

where M is a metal ion, L is the ligand, usually the anion. \( M \text{M} \text{L}^n \) is the complex ion formed by the interaction of the metal and the ligand.

If the initial molar concentration of M is C and that of L is \( C' \) then the ratio \( C'/C \) is denoted by P. If x ml. of the ligand are mixed with \((1-x)\) of the metal assuming no
contraction or expansion in volume and if $c_1$, $c_2$ and $c_3$ be the respective molar concentrations of $M$, $L$ and $M \cdot L$ in the resulting solution at equilibrium the dissociation constant $K_d$ of the complex (reciprocal of the stability constant) can be represented as follows:

\[ c_1^m + c_2^n = K_d c_3 \]  \hspace{1cm} (2)

\[ c_1 + nc_3 = C(1-x) \]  \hspace{1cm} (3)

\[ c_2 + nc_3 = pCx \]  \hspace{1cm} (4)

Equations 3 and 4 are obtained by equating the total quantities of $M$ and $L$ respectively. Now substituting the values for $c_1$ and $c_2$ in the equation (1) we get:

\[ \left\{ \frac{C(1-x)}{1 + nc_3} \right\}^m \left\{ pCx - nc_3 \right\}^n = K_d c_3 \]  \hspace{1cm} (5)

The concentration, $c_3$, of the complex, therefore, depends only on the value of $x$ (composition of the mixture) and it will have a maximum value when

\[ \frac{dc_3}{dx} = 0 \]

On differentiating the equation (5) with respect to $x$ where $p$, $c$, $m$, $n$ and $K_d$ are constants and putting the value $\frac{dc_3}{dx} = 0$ in the resulting equation we get on simplification for $c_3$

\[ c_3 = \frac{pC \left( n-(m+n)x \right)}{(p-1) mn} \]  \hspace{1cm} (6)

The values of $c_1$, $c_2$ and $c_3$ from equation 3, 4 and 6 respectively are substituted in equation 2 and the terms are rearranged; as a result the following equation is obtained:

\[ c_3^{m+n-1} \left\{ \frac{(p_m+n)x-n}{m+n} \right\}^{m+n} = K_d \left[ m^{n-1} n^{m-1} (p-1)^{m+n-1} \left\{ n-(m+n)x \right\} \right] \]  \hspace{1cm} (7)
If the isomolar solutions of the metal and the ligand are used, \( P = 1 \). In such a case the right hand side of the equation (7) becomes 0. Now on equating the left hand side of the equation to zero and rearranging the terms we get:

\[(m+n) x - n = 0; \text{ or } \frac{m}{n} = 1 - \frac{x}{x} \quad \ldots \quad (8)\]

From equation (8) it is clear that the composition of the complex \( \frac{m}{n} \) can be determined given that the ratio of the volumes of the solutions of \( M \) and \( L \), \( 1 - \frac{x}{x} \), which represents the maximum formation of the complex is experimentally determined. The simple values of \( m \) and \( n \) are to be taken for the determination of the formula of the complex. The values thus obtained are independent of the dissociation constant of the complex and the molar concentration of \( M \) and \( L \) chosen for the purpose. It is assumed here that in dilute solutions only mono-nuclear complexes will be present and hence the single values of \( m \) and \( n \) give the stoichiometric formula of the complex.

In case non-isomolar solutions are employed initially \( x \) depends both on the concentration of the primary solutions and on the dissociation constant \( K_d \). In this case the equation (7) can be used for determining the dissociation constant. For the complex with stoichiometric ratio 1:1 \( m \) and \( n \) are each equal to one and accordingly the equation can be written in a simplified form:

\[ K_d = C \left( \frac{(P+1)x-1}{(P-1)(1-2x)} \right)^2 \quad \ldots \quad (9) \]

The values of \( C \) and \( P \) are known from the initial concentrations of \( M \) and \( L \). If the value of \( x \), the volume fraction
of L where the maximum amount of complex is formed (or \( c_3 \) is maximum) is determined experimentally the dissociation constant can be evaluated. The reciprocal of this i.e. the stability constant may be obtained therefrom. Job proposed to study the function of \( x \) of any molecular property which obeys the laws of mixtures.

If \( P \) is the additive molecular property being studied then its observed value at equilibrium can be written according to the mixture law:

\[
P(\text{observed}) = c_1 P_A + c_2 P_B + c_3 P_{AM} B_n \cdots \cdots (10)
\]

In case \( A \) and \( B \) do not react to give a complex ion the observed value of \( P \) for a mixture of solutions is given by the equations:

\[
P_{AB} = (1-x) C_P A + PC_x P_B \cdots \cdots \cdots \cdots (11)
\]

If the differences between the calculated value of the property for no reaction \((P_{AB})\) and its value as observed in the case of complex formation \( P \) (obs) is denoted by \( Y \) then:

\[
Y = P_{AB} - P \text{ (obs)} = (1-x) C_P A + PC_x P_B - (c_1 P_A + c_2 P_B + c_3 P_{AM} B_n) \cdots \cdots (12)
\]

Substituting the values of \( c_1 \) and \( c_2 \) from equation (3) and (4) respectively in the above equation (12) we obtain:

\[
Y = c_3 (m_P A + n_P B - P_{AM} B_n) \cdots \cdots \cdots (13)
\]

Differentiation of this with respect to \( x \) gives:

\[
\frac{dY}{dx} = (m_P A + n_P B - P_{AM} B_n) \frac{dc_y}{dx} \cdots \cdots (14)
\]

It is quite clear from the above equation that \( dY/dx = 0 \) when \( dc_y/dx = 0 \). Thus when the concentration \( c_3 \) of the complex is at maximum, \( Y \) must have its extremum value. \( Y \) will be maximum or minimum depending on
\[ n_P^A + n_P^B \geq P_{ABn}. \]

It becomes evident from the above mathematical treatment that by choosing a suitable additive molecular property and studying \( Y \) as the function of \( x \) (by plotting the value of \( Y \) against the corresponding value of \( x \)) it is possible to get the value of \( x \) where \( Y \) is extrema and this value of \( x \) represents the point where \( c_3 \) is maximum, (i.e. maximum complex is formed). At this point where \( c_3 \) is maximum, composition \((m/n)\) of the complex can be derived from the ratio of the two solutions.

Job's method provides a simple means for studying the complex ions especially where only one complex exists in the system. Job (19, 36) chose molar extinction coefficient as the index property for spectrophotometric study of the complex system. This widely applicable method has been critically examined by a number of workers who have pointed out its merits and demerits.

The limitations and weaknesses of this method have been discussed by Wouldbye (37), Jones (38), Rossotti and Rossotti (39), Jones and Innes (35). Critics of this method all agree that this can be successfully applied to establish the composition of the complex where only one complex is formed. The present ill repute of this method according to Jones (38), is due to its application in simple form to systems where more than one complexes are formed which has also been discussed by Wouldbye (37). Jones adds that the method of continuous variation can be used to establish the
stoichiometry of a single complex in many systems. Sommer and Hnilickova (40), Asmus (41) and Watkins and Jones (42) are the other authors among the critics of the method. They are sceptical about the results obtained by this method by using properties other than absorbance measurements.

An extension of this method to investigate the systems where two or more complex species are present has been discussed by Vosburgh et al (20, 43) but a more general treatment has been given by Katsin and Gebert (44).

Ernst and Menashi (28) have discussed the theoretical principles underlying the spectrophotometric method of continuous variation. They conclude that among, the various index properties used optical density is the most successful property. A method has been devised by them where the continuous variation data can be directly used to determine the stability constants in some cases.

Various workers (19, 20, 44-50) have used this method for determining the stability constants. Most of them have devised it to use only when a single complex is formed and two (49, 50) of them opine that it can be used when additional equilibria play an important role. For a system with only one complex good results are obtained. Watkins and Jones (42) have pointed out that with proper mathematical treatment for the systems containing two or more complex ions, without any simplification, it can give more accurate results than generally expected.

With all its limitations the method still enjoys the
popularity for studying the single complex systems (51-53).

(11) Vosburgh and Cooper method:

Job (54) himself, after noting De Wij's (55) work, had shown that the method of continuous variation was not generally applicable when more than one compounds are formed in the system. This led the authors Vosburgh and Cooper (20) to examine this method and see if it could be applicable to the systems where more than one complexes are formed. Theoretically, by giving the mathematical treatment, these authors have proved that the method of continuous variation could be used to ascertain whether or not more than one complexes are formed from a pair of given components. Further they suggested that it is possible to study more than two complexes in a system by light absorption measurements, if proper selection of wave lengths is made to study the different compounds formed.

According to the method suggested, it is only necessary to make measurements with a variety of wave lengths, covering the region of the spectrum absorbed. If only one single compound is formed $Y$ should be a maximum at a fixed value of $X$ regardless of the wave length employed, provided that the extinction coefficient of the chelate compound differs from that of the coloured reactant. By using several wave lengths for measurements it is possible to determine whether or not more than one compounds are formed in the system. They applied this method during their investigation of Ni ion and O-phenanthroline. They mixed the solutions of the two
components in various proportions and the optical density was measured at a number of wave lengths. If the optical measurements at all the wave lengths led to the same result i.e. superimposable curves are obtained by plotting absorbance against wave length, it can be concluded that only a single compound is formed in the system.

Yoe and Harvey (Jr)\(^{(56)}\) applied this method for the investigation of iron complex with 4-hydroxy-biphenyl-3-carboxylic acid. They mixed the isomolar solutions of the components in the following ratios (Reagent to iron) 0.2:1; 0.5:1; 1:1; 2:1; 3:1 and 9:1, volume being kept constant and measured the absorbance between 520 to 620 mp at the interval of 10 mp. By plotting log E versus wave length they got curves identical in shape which could be superimposed on each other on adding a suitable constant to the ordinate of each curve, thus proving the existence of only one complex in the system.

One exception suggested to this method is that the formation of a colourless compound may be overlooked if formed in addition to the coloured one.

Vosburgh and Cooper have discussed the mathematical basis for the method in their original paper (20).

(iii) Molar ratio method:

The credit of devising this method for the investigation of the empirical formulae of the coloured complexes in solution goes to Yoe and Jones (21). They have assumed the reaction between the two components according to the equation
A + nB = ABₙ. 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 (57). 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 the modification of the molar ratio method has been suggested by Harvey and Manning (25, 58) where they have suggested the adjustment of ionic strength with the addition of a indifferent electrolyte. This method in general is termed as spectrophotometric titration.

Mayer and Ayres (59) have mathematically calculated the possibility of applying this method to a system where more than one complex exist. According to them the method in the modified form provides a more positive indication for the absence of any spectrophotometrically distinguishable complex.

Nayar and Pande (3 a) applied a similar method using conductance as the index property to determine the empirical
formula of the complex present in solution. They have termed this method as monovariation method.

In the present investigations, the three methods detailed above have been chosen in order to study the systems and to establish the stoichiometric formulae for the complexes present therein. Molar ratio method has also been employed to investigate the formation of a complex in a particular system at different pH. This is to confirm as to whether or not only one complex is formed at different pH ranges.

Job's method of continuous variation has been followed for calculating the stability constants of the chelates as it has been conclusively proved that under the experimental conditions here only one complex is present in each system.

It has been mentioned that the dye-metal chelate systems under consideration here, are all coloured and therefore light absorption was chosen to be the index property. Moreover it has been well established, according to many authors, (Loc-cit) that light absorption is the only property which gives reliable and convincing results by continuous variation method. It is for this reason that spectrophotometric investigations were undertaken. To corroborate the results obtained by continuous variation method, Vosburgh and Cooper method and molar ratio method were also applied.
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