
PART - TWO

***pH-METRIC DETERMINATIONS OF STABILITY
CONSTANTS OF GUANYLHYDRAZONE COMPLEXES
WITH SOME METAL IONS***

CHAPTER - V
INTRODUCTION

5.1 INTRODUCTION

Introduction of modern instruments, compilation of important data and use of new computation methods enabled the chemists to arrive at useful clues about structural aspects and reactivities of inorganic systems. The tremendous growth of literature in the field of solution equilibria has significantly important place in the progress of inorganic chemistry. The subject has a very wide scope and has numerous applications.

Formation of chelate molecule is interesting from synthetic, analytical and theoretical point of view. Chelate formation requires certain favourable structural features. The chelate molecules have certain properties which attract to structural chemists, biochemists and technologists. Such a wide scope naturally demands thorough understanding of process of chelation.

Isolation of a well characterisable single compound in a pure form has very much importance. The synthetic chemists can not ignore the existence of complexes or chelate species in the solution phase. The synthetic methods of inorganic chemistry and investigation of structure and nature of complex species present in a solution, when ligand is added to metal ion is very much interesting from the research point of view.

The present work covers the experimental work on solution equilibria between metal ions and some substituted guanylhydrazones in ethanol-water media.

The attempts have been made to analyse the experimental data and to bring out some interesting aspects of equilibria involved in the chosen systems.

5.2 FORMATION CONSTANTS AND THEIR DETERMINATION

The chemists are mainly interested in the interactions between different types of molecules. In a homogeneous solution medium, these interactions are often complicated. Hence, the structures of species involved, the extent of formation of each species and their further tendencies to undergo chemical changes must be carefully studied. The thermodynamic parameters of ionic equilibria are important. The equilibrium constants of a number of systems are studied by using different methods. Usually a solution of a metal ion and ligand are mixed and after equilibration the concentrations of each of the species in the solution are then measured.

Consider a system containing A and B as reactants which gives C as a product.



If the concentrations of the reactants and the products are known, equilibrium constant can be calculated.

$$K_c = \frac{[C]}{[A][B]} \quad \dots\dots(5.1)$$

Where K_c is the equilibrium constant. Species in brackets represent their concentrations in moles per litre. In a simple system, measurements can be carried out by knowing initial and final concentrations of species A and B only. The amount of C can be determined from the difference in the initial and final concentrations of A and B. When the system is very complicated, but has theoretical, applied or analytical importance, the computation techniques using computer programmes are used.

The measurements of equilibrium concentrations of the species are rather difficult, since the measurements should not disturb the equilibrium. The second difficulty in determination of equilibrium constant is that, it depends on the activities rather than on concentrations. This difficulty can overcome by keeping the concentrations of all the species low, as the activities and concentrations are numerically almost equal in very dilute solutions. In second approach, stability constant can be determined by using 'non-complexing' salt environment by adding salt such as NaClO_4 . It gives ions Na^+ and ClO_4^- . The deviations from unit activity are mainly due to Na^+ and ClO_4^- ions. Stability constants in a series of solutions containing different amounts of salts is determined. By extrapolation to zero salt concentration stability constant is determined, where activity coefficients are unity.

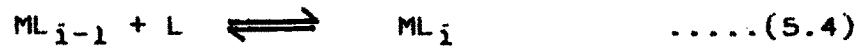
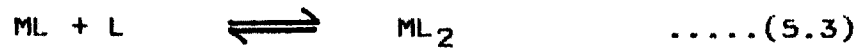
Complex formation between a metal ion and ligand involves competition between metal ions and protons. Most ligand species act as Lewis bases and form complexes with metal ions. They also act as Bronsted bases and hence combine with hydrogen ions. The competition between metal ions and protons for ligand allow us to measure the concentrations of L at equilibrium. But this situation has the disadvantage of increasing the number of different species which are present in solution.

5.3 FORMATION CONSTANT

When a metal ion M reacts with ligand L, in a homogeneous medium at a given temperature, reaction may lead to a series of reactions involving several stepwise dynamic equilibria, finally leading to formation of stable complex or chelate.

Generally, metal ion is shown by M^{n+} , monoprotic ligand as HL and ligand ion as L^- , polyprotic ligand as H_mL and ligand ion as L^{m-} . For convenience, the charges are omitted.

If N is the maximum number of ligand, ions which can coordinate to metal ion, then series of equilibria involved during formation of chelate can be shown as



For each of the above steps in the stepwise process, the equilibrium constant can be defined as

$$K_i^T = \frac{a. ML_i}{a. ML_{i-1} \cdot aL} \quad \dots\dots(5.6)$$

Where K_i^T = i^{th} thermodynamic metal-ligand stability constant i.e. formation constant for equilibrium as shown in (5.4), and a = activity of each species involved.

The relation between thermodynamic stability constant and stoichiometric stability constant is

$$K_i^T = K_i^C \times \frac{fM \cdot fL_i}{f ML_i} \quad \dots\dots(5.6)$$

Where f represents activity coefficients of the respective species.

It is assumed that at low ionic strength, the activity and concentration are the same. So at low concentration, equation (5.6) becomes,

$$K_i^C = \frac{[ML_i]}{[ML_{(i-1)}] [L]} \quad \dots\dots(5.8)$$

Where [] represents concentration of different species in moles per litre.

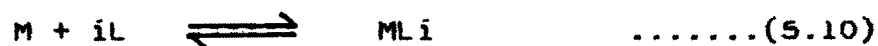
K_i^c = i^{th} stoichiometric metal-ligand stability constant.

Let, $K_1, K_2, K_3 \dots, K_{i-1}$ and K_i are successive stepwise stability constants, and β_i is overall metal-ligand stability constant, then

$$\beta_i = K_1 \times K_2 \times K_3 \times \dots \times K_{i-1} \times K_i$$

$$= \sum_{i=1}^i K_i \quad \dots\dots(5.9)$$

Let us consider, overall metal-ligand reaction,



Hence, in dilute solution,

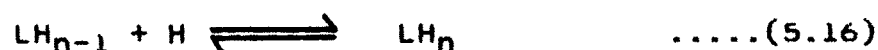
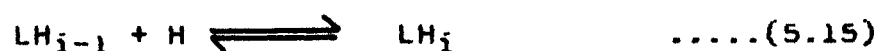
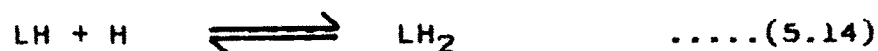
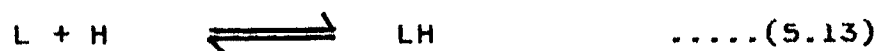
$$\beta_i = \frac{[ML_i]}{[M] [L]^i} \quad \dots\dots(5.11)$$

Equating equation No. (5.9) and (5.11), we get

$$\beta_i = \frac{[ML_i]}{[M] [L]^i} = \sum_{i=1}^i K_i \quad \dots\dots(5.12)$$

5.4 FORMATION CONSTANT OF THE LIGAND i.e. PROTON-LIGAND STABILITY CONSTANT

The metal-ligand stability constant is determined by working out metal-ligand system. In the similar way, proton-ligand stability constant i.e. formation constants of the ligands can be determined. Ligand ion may interact with proton. The stepwise protonation of ligand can be shown as



For simplicity, the charges on all the species are neglected.

The corresponding equation for the thermodynamic formation constant can be represented by general equation.

$$K_{iH}^T = \frac{a. LH_i}{a. LH_{i-1} . a.H} \quad \dots\dots(5.17)$$

Where, K_{iH}^T represents i^{th} thermodynamic proton-ligand stability constant.

a = activities of corresponding species.

But in reality we know concentrations of the species. In dilute solution, concentration and activity are same. Hence, stoichiometric proton-ligand stability constant becomes

$$K_{iH}^c = \frac{[LH_i]}{[LH_{i-1}] [H]} \quad \dots\dots(5.18)$$

[] represents concentration in moles per litre.

When the ligand is completely protonated, then corresponding proton-ligand stability constant is represented by β_iH which is obtained by equation.

$$\beta_i H = \frac{[LH_i]}{[L][H]^i} = \sum_{i=1}^i K_i \quad \dots\dots(5.19)$$

It is assumed that only those species which are present in above equilibria are present in solution. The species like polynuclear complexes, unionised metal salts, complexes containing hydroxyl groups and complexes containing protons in addition to ligands are not present.

n and nA

The most important term in solution equilibria introduced by J.Bjerrum¹, \bar{n} , is defined as the average number of ligand molecules bound per metal ion; mathematically,

$$\bar{n} = \frac{\text{Total concentration of ligand bound to metal}}{\text{Total concentration of metal}}$$

$$\therefore \bar{n} = \frac{\sum_{i=0}^N i [ML_i]}{\sum_{i=0}^N [ML_i]} \quad \dots\dots(5.20)$$

We know that

$$ML_i = K_i [ML_{i-1}] [L]$$

Substituting this value in equation (5.20) and eliminating [M], we get,

$$\bar{n} = \frac{K_1 [L] + 2K_1 K_2 [L]^2 + \dots + NK_1 K_2 \dots K_N [L]^N}{1 + K_1 [L] + K_1 K_2 [L]^2 + \dots + K_1 K_2 \dots K_N [L]^N} \quad \dots\dots(5.21)$$

But, we know that

$$\beta_i = \beta_1 \times \beta_2 \times \beta_3 \times \dots \times \beta_{i-1} \times \beta_i$$

Putting this value in above equation, we get

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \dots + N\beta_N [L]^N}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_N[L]^N} \quad \dots(5.22)$$

$$\text{i.e. } \bar{n} = \frac{\sum_{i=0}^N i\beta_i[L]^i}{\sum_{i=0}^N \beta_i[L]^i} \quad \dots(5.23)$$

J. Bjerrum called above equation as formation function. This equation is used to found \bar{n} .

In the similar way, formation function equation for \bar{n}_A can be obtained. \bar{n}_A is defined as the average number of protons bound per not-complex-bound ligand molecules.

$$\therefore \bar{n}_A = \frac{K_1^H[H] + 2K_1^H K_2^H [H]^2 + \dots + jK_1^H K_2^H \dots K_j^H [H]^j}{1 + K_1^H[H] + K_1^H K_2^H [H]^2 + \dots + K_1^H K_2^H \dots K_j^H [H]^j} \quad \dots(5.24)$$

$$\text{But } \beta_n = K_1 K_2 \dots K_N$$

Putting this value in above equation, we get

$$\bar{n}_A = \frac{\beta_1^H[H] + 2\beta_2^H[H]^2 + \dots + j\beta_j^H [H]^j}{1 + \beta_1^H[H] + \beta_2^H[H]^2 + \dots + \beta_j^H[H]^j} \quad \dots(5.25)$$

$$\text{i.e. } \bar{n}_A = \frac{\sum_{i=0}^J i \beta_i^H [H]^i}{\sum_{i=0}^J \beta_i^H [H]^i} \quad \dots\dots(5.26)$$

$$\text{and } \beta_0^H = 1$$

The total amount of metal ion concentration and total amount of ligand concentration in solution are as shown below.

$$T^*_M = \sum_{i=0}^N [ML_i] \quad \dots\dots(5.27)$$

$$\text{and } T^*_L = \sum_{i=0}^J [LH_i] + \sum_{i=0}^N i [ML_i] \quad \dots\dots(5.28)$$

But, we know that

$$ML_i = K_i [ML_{i-1}] [L]$$

Using this value in equation (5.27), we get

$$T^*_M = M \sum_{i=0}^N \beta_i [L]^i \quad \dots\dots(5.29)$$

$$\text{Similarly, } LH_i = [L] \beta_i^H [H]^i$$

Putting this value in equation (5.28), we get

$$T^*_L = L \sum_{i=0}^J \beta_i^H [H]^i + M \sum_{i=0}^N i \beta_i [L]^i \quad \dots\dots(5.30)$$

The concentration of ligand not bound to metal is

$$T^*_L = n T^*_M \quad \dots\dots(5.31)$$

Substituting the value of T^*_L and T^*_M in above equation, we get

$$T^*_L - nT^*_M = L \sum_{i=0}^j \beta_i^H [H]^i + M \sum_{i=0}^N i\beta_i [L]^i - nM \sum_{i=0}^N \beta_i [L]^i \quad \dots(5.32)$$

$$\therefore T^*_L - nT^*_M = L \sum_{i=0}^j \beta_i^H [H]^i \quad \dots\dots(5.33)$$

$$\therefore L = \frac{T^*_L - nT^*_M}{\sum_{i=0}^j \beta_i^H [H]^i} \quad \dots\dots(5.34)$$

Taking log of both sides, we get

$$\log L = \log (T^*_L - nT^*_M) - \log \sum_{i=0}^j \beta_i^H [H]^i \quad \dots\dots(5.35)$$

$$\therefore PL = \log \frac{\sum_{i=0}^j \beta_i^H [H]^i}{(T^*_L - nT^*_M)} \quad \dots\dots(5.36)$$

5.5 DETERMINATION OF STABILITY CONSTANTS

The determination of stability constant is reviewed by Martel and Calvin², Martel³, Irving and Rossotti⁴, Rossotti and Rossotti⁵, Lewis and Wilkins⁶ and Sillen and Martel⁷.

Following experimental methods are used for determination of stability constant.

Potentiometry, polarography, spectrophotometry, vibration spectroscopy, N.M.R. spectroscopy, e.s.r. spec-

trospectroscopy, spectropolarimetry, colorimetry, solvent extraction, solubility measurements, viscometry, reaction kinetics, x-ray studies, coagulation studies, Mossbauer studies etc. In these methods following three steps are normally present.

- (1) Formation curve is obtained from experimental measurements.
- (2) Formation curve is used to determine stoichiometric stability constant.
- (3) By extrapolation to zero ionic strength the thermodynamic stability constant is obtained from the stoichiometric stability constant at given temperature and at various ionic concentrations.

5.6 pH-METRIC METHOD FOR DETERMINATION OF THE FORMATION CONSTANT

The pH-metric method involves the measurement of H^+ ion concentration by using a pH-meter. The measurement by pH-meter does not disturb the equilibrium, and hence it is a popular and widely used method. This method is proper for those chelates which are soluble either in water or mixed organic solvents. Water-dioxane, water-methanol and water-ethanol mixed organic solvents can be used, but the pH measurement in such media must be corrected by using appropriate corrections⁸.

In the present study, pH-metric method is used for measurements, which are used for determination of formation curve from which stability constant is determined. These formation curves are obtained by Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti⁴.

The method of Irving and Rossotti⁴

In this method, the stability constants were determined by pH-meter. The readings of pH-meter in 50 % ethanol-water v/v were corrected for solvent effect by applying previously reported correction⁸.

In this method, series of titrations are carried out with standard alkali solution. Extreme care should be taken for purification of solvent and preparation of standard solutions. Standard stock solution of strong alkali must be carbonate free. Following three types of titrations were carried out.

- (1) Standard HClO_4 solution Vs. standard NaOH solution.
- (2) [Standard HClO_4 solution + known amount of standard ligand solution] Vs. NaOH solution.
- (3) [Standard HClO_4 solution + known amount of standard ligand solution + known amount of metal ion solution] Vs. standard NaOH solution.

In all these titrations, solvent composition and final volume was kept constant. During titration, the temperature was controlled within $\pm 0.1^\circ\text{C}$ by using thermostat. The mixed solution is stirred by magnetic stirrer before each reading. The mixed solution used for titration acts as an electrolyte. The cell used for the measurement contains two half cells. Calomel electrode acts as a reference electrode and the glass membrane electrode as a response electrode.

These measurements were used to draw the formation curves. The first titration curve is characteristic of strong acid-strong base titration, which is a sigmoid type.

In the second curve, there is a slight drooping in the upper portion of the sigmoid curve. Drooping in the curve is due to ligand which is weakly acidic in nature. In this titration, the ligand molecule get deprotonated with addition of base. This curve is used to determine nA and the proton-ligand stability constants. If ligand contains two or more ionizable protons, their corresponding pK_1 and pK_2 values can be determined provided that the protons are released before the pH value goes to reasonably high limit i.e. upto pH 13.

The third curve is a more drooping sigmoid curve, as metal abstracts the proton from the ligand. Thus pH of

the titrated solution for the corresponding volume of NaOH will be lower than ligand and acid titrations. Drooping of the third titration curve indicates the formation of complex or chelate. By using these curves metal-ligand stability constant is determined.

In the mixed solvent, the relation between pH-meter reading and stoichiometric hydrogen ion concentration is given by Van Uitert and Hass¹⁰ as

$$- \log [H^+] = \text{pH} + \log f_H + \log U^*_H \quad \dots\dots(5.37)$$

Where, f_H = activity coefficient of H^+ in organic solvent-water mixture at constant temperature

U^*_H = correction factor at zero ionic strength.

By taking antilog of quantities on both sides (eq.5.37) and rearranging we get,

$$\frac{1}{\text{antilog pH}} = f_H [H] U^*_H \quad \dots\dots(5.38)$$

$$\therefore [H] = \frac{1}{f_H U^*_H} \cdot \frac{1}{\text{antilog pH}} \quad \dots\dots(5.39)$$

On putting the value of $[H]$ in equations (5.24) and (5.25), we get

$$\frac{K_1^H}{(f_H U^*_H)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{2 K_1^H K_2^H}{(f_H U^*_H)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots + \frac{j K_1^H K_2^H \dots K_j^H}{(f_H U^*_H)^j} \left[\frac{1}{\text{antilog pH}} \right]^j$$

$$\bar{n}_A = \frac{\dots}{\dots} \dots (5.40)$$

$$1 + \frac{K_1^H}{(f_H U^*_H)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{K_1^H K_2^H}{(f_H U^*_H)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots + \frac{K_1^H K_2^H \dots K_j^H}{(f_H U^*_H)^j} \left[\frac{1}{\text{antilog pH}} \right]^j$$

But, $\beta_n = K_1 \times K_2 \times \dots \times K_n$

$$\frac{\beta_1^H}{(f_H U^*_H)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{2\beta_2^H}{(f_H U^*_H)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots + \frac{j\beta_j^H}{(f_H U^*_H)^j} \left[\frac{1}{\text{antilog pH}} \right]^j$$

$$\therefore \bar{n}_A = \frac{\dots}{\dots} \dots (5.41)$$

$$1 + \frac{\beta_1^H}{(f_H U^*_H)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{\beta_2^H}{(f_H U^*_H)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots + \frac{\beta_j^H}{(f_H U^*_H)^j} \left[\frac{1}{\text{antilog pH}} \right]^j$$

Irving and Rossotti define proton-ligand formation constant or ionisation constant as:

$$pK_i^H = \frac{K_i^H}{f_H U^*_H} \dots\dots\dots(5.42)$$

$$\therefore K_i^H = f_H U^*_H pK_i^H \dots\dots\dots(5.43)$$

and

$$p\beta_i^H = \frac{\beta_i^H}{[f_H U^*_H]^i} \dots\dots\dots(5.44)$$

$$\therefore \beta_i^H = [f_H U^*_H]^i p\beta_i^H \dots\dots\dots(5.45)$$

Determination of \bar{n}_A , \bar{n} and pL

\bar{n}_A , \bar{n} and pL can be calculated by using the equations (5.24), (5.21) and (5.36) respectively. But these equations required concentration of H ions i.e. [H]. Titration curves are obtained by titrating mineral acid and ligand, in presence or absence of metal ions. Then in more acidic solutions, [Na] and [OH] are negligible and $E \gg TL$. Hence, $[H] \approx E$. The calculated value of $T_H - [H]$ are sensitive to [H]. Thus small error may give ridiculous results. This difficulty can be overcome by using following method.

The points on the acid curve are obtained by equation. $[H'] = E' + [OH'] - [Na'] \dots\dots\dots(5.46)$

Similarly, points for mixture of mineral acid and ligand curve are obtained as

$$[H''] = E'' + [OH''] - [Na''] + YTL'' - \bar{n}A^2 \dots\dots(5.47)$$

Here, YT_L'' is the number of dissociable protons for complex formation in gram ions per litre.

Let pH-meter readings be the same for both solutions, then

$$[OH'] = [OH''] \quad \dots\dots(5.48)$$

and $[H'] = [H'']$ \dots\dots(5.49)

Then, we get

$$nA'' = \left\{ \frac{(E'' - E') - ([Na''] - [Na']) + YT_L''}{T_L''} \right\} \dots\dots(5.50)$$

Let us consider,

V^* = Initial volumes

E^* = Mineral acid concentrations

T_L^* = Total ligand concentration are same in each titration

V' and V'' are the volumes of alkali solution of concentration N' , required to reach the points $[Na']$ and $[Na'']$

Hence,

$$E' = \frac{V^* E^*}{(V^* + V')} \quad \dots\dots(5.51)$$

$$E'' = \frac{V^* E^*}{(V^* + V'')} \quad \dots\dots(5.52)$$

$$[Na'] = \frac{V' N'}{(V^* + V')} \quad \dots\dots(5.53)$$

$$[Na''] = \frac{V'' N'}{(V^* + V'')} \quad \dots\dots(5.54)$$

Using these values in equations (5.50), we get

$$\bar{nA} = \frac{YT_L^* + \frac{(V^* - V'')(N' + E^*)}{V^* + V'}}{T_L^*} \quad \dots(5.55)$$

This equation is used to determine \bar{nA} for proton-ligand stability constants in the present study.

The curves obtained for mixture of mineral acid, ligand and metal ions are used to determine metal-ligand stability constants. The [H] concentration on metal ion curve for any point is obtained by equation,

$$[H'''] = E''' + YT_L''' - [OH'''] - [Na'''] - \bar{nA}''' T_L''' \bar{n}''' T_M''' \quad \dots(5.56)$$

When ionic strength is kept constant, the pH-meter readings are same. Hence,

$$[H''] = [H'''] \quad \dots\dots\dots(5.57)$$

$$[OH''] = [OH'''] \quad \dots\dots\dots(5.58)$$

and $\bar{nA}'' = \bar{nA}''' \quad \dots\dots\dots(5.59)$

Then,

$$\bar{n}''' = \frac{(E'' - E''') + (T_L'' - T_L''')(Y - \bar{nA}'') - (Na'' - Na''')}{\bar{nA} \cdot T_M} \quad \dots(5.60)$$

If both the solutions have initial volume V^* and concentrations of acid and ligand are E^* and T_L^* respectively, and V'' and V''' are volumes of alkali of concentration N' required to add so as to reach points Na'' and Na''' , then above equation becomes

$$\bar{n}''' = \frac{(v''' - v'') (N'' + E'') + T^*_L (Y - \bar{n}A'')}{(v^* + v'') \bar{n}A''' \cdot T^*_M} \quad \dots(5.61)$$

The equation (5.30) can be rewritten by using equation (5.26).

$$T_L''' = [L'''] \sum_{i=0}^j \beta_i^H [H''']^i + \bar{n}''' T_M''' \quad \dots(5.62)$$

where, $\beta_i^H = 1$

$$\frac{1}{[L''']} = \frac{\sum_{i=0}^j \beta_i^H [H''']^i + \bar{n}''' T_M''' - T_L'''}{[L''']} \quad \dots(5.63)$$

Taking logarithm on both sides, we get

$$pL = \log \left\{ \frac{\sum_{i=0}^j \beta_i^H [H''']^i}{T_L''' - \bar{n}''' T_M'''} \right\} \quad \dots(5.64)$$

The equation (5.64) can be rewritten, using equations (5.38), (5.40), (5.43) and (5.45) as

$$pL = \log \left\{ \frac{\sum_{i=0}^j \beta_i^H \left[\frac{1}{\text{antilog pH}} \right]^i}{T^*_L - \bar{n}''' T^*_M} \times \frac{v^* + v''}{v^*} \right\} \quad \dots(5.65)$$

$$\therefore pL = \log \left\{ \frac{1 + \beta_1^H \left[\frac{1}{\text{antilog pH}} \right]}{T^*_L - \bar{n}''' T^*_M} \times \frac{v^* + v''}{v^*} \right\} \quad \dots(5.66)$$

Where, $\gamma = 1$

$$pL = \log \left\{ \frac{1 + pK_1 \left[\frac{1}{\text{antilog } pH} \right] + pK_1 pK_2 \left[\frac{1}{\text{antilog } pH} \right]}{T^*L - T^*M \bar{n}'''} \right\} \times \frac{v^* + v''}{v^*} \quad \dots (5.67)$$

Where $\gamma = 2$

By using above equations, values of \bar{n} and pL are calculated, from which stability constant of complex compound can be determined.

5.7 DETERMINATION OF STABILITY CONSTANTS FROM THE FORMATION CURVES

Formation constant is considered through various angles. There are different methods which can be used for determination of stability constants. Here, some of the important methods are discussed.

Method 1 - Graphical Method

In present study, for determination of stability constants, this method is used.

Let us consider the equation,

$$\bar{n} = \frac{K_1 [L]}{1 + K_1 [L]}$$

$$\therefore \bar{n} + \bar{n} K_1 [L] = K_1 [L]$$

$$\begin{aligned} \therefore \bar{n} &= K_1 [L] - \bar{n} K_1 [L] \\ &= K_1 [L] (1 - \bar{n}) \end{aligned}$$

$$\therefore \frac{1}{[L]} = K_1 \cdot \frac{(1-\bar{n})}{\bar{n}}$$

Taking logarithm on both sides, we get

$$pL = \log K_1 + \log \frac{(1-\bar{n})}{\bar{n}} \quad \dots(5.68)$$

The plot of $\log \frac{(1-\bar{n})}{\bar{n}}$ vs. pL is a straight line

$$\text{When } \log \frac{1-\bar{n}}{\bar{n}} = 0$$

$$pL = \log K_1$$

Similarly, $\log K_2$ can be obtained by equation

$$pL = \log K_2 + \log \frac{(2-\bar{n})}{(\bar{n}-1)} \quad \dots\dots(5.69)$$

$$\text{When } 2-\bar{n} = \bar{n}-1$$

$$pL = \log K_2$$

Method 2 - Bierrum's Method

In this method, stability constant is obtained by solving simultaneous equations.

Let us consider equation.

$$\sum_{n=0}^N (n-n)\beta_n [L]^n = 0 \quad \dots\dots(5.70)$$

Sullivan and Hindman¹¹ solved this equation by determinant method.

$$\begin{vmatrix} (\bar{n}-1) [L_1] + \dots + (\bar{n}_N - N) [L_1]^N \\ (\bar{n}-1) [L_N] + \dots + (\bar{n}_N - N) [L_N]^N \end{vmatrix} \neq 0$$

By solving above determinant, N linear simultaneous equations are obtained from which N stability constants for ML_1, ML_2, \dots, ML_N complexes can be determined.

Let us consider equation when $N=2$.

$$\bar{n} + (\bar{n}-1) K_1 [L] + (\bar{n}-2) K_1 K_2 [L]^2 = 0 \quad \dots(5.71)$$

and
$$\bar{n} + (\bar{n}-1) \beta_1 [L] + (\bar{n}-2) \beta_2 [L]^2 = 0 \quad \dots(5.72)$$

The values of \bar{n} and $[L]$ can be experimentally determined while values of β_1 and β_2 are not known. Two equations are then used to find β_1 and β_2 .

The values of K_1 and K_2 are obtained by using equation (5.71).

$$K_1 = \frac{1}{[L]} \cdot \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n}) K_2 [L]} \quad \dots(5.73)$$

and

$$K_2 = \frac{1}{[L]} \cdot \frac{\bar{n} + (\bar{n}-1) K_1 [L]}{(2-\bar{n}) K_1 [L]} \quad \dots(5.74)$$

Same procedure is used to determine N values of stability constants.

Method 3 - Interpolation of Half Integral Values

This is second method which is used in this present work. The values of K_1 & K_2 as obtained in method 2, give the following type of equations.

$$\log K_1 = pL \ 1/2 + \log \left[2 / (1 + \sqrt{1 + 12K_2/K_1}) \right] \quad \dots(5.75)$$

and

$$\log K_2 = pL \ 3/2 + \log \left[2 / (1 + \sqrt{1 + 12K_2/K_1}) \right] \quad \dots(5.76)$$

Where $pL \ 1/2$ and $pL \ 3/2$ are free ligand exponent when $\bar{n} = 0.5$ and 1.5

when $K_{n-1} \gg K_n$, then

$$ML_{n-1} \approx ML_n$$

In this case, contribution of other species such as ML_{n-2} and ML_{n+1} are neglected.

When K_2/K_1 is very small, then

$$\sqrt{1 + 12K_2/K_1} \approx 1.$$

$$\therefore \log K_1 = pL \ 1/2 \quad (\because \log 1 = 0) \quad \dots(5.77)$$

similarly,

$$\log K_2 = pL \ 3/2 \quad \dots(5.78)$$

In general, we get

$$\log K_i = pL(i - 1/2) \quad \dots(5.79)$$

Thus, $\log K_1, \log K_2, \dots, \log K_i$ which are corresponding to ML_1, ML_2, \dots, ML_n are obtained at $\bar{n} = 0.5, 1.5, 2.5, \dots, (n-0.5)$ respectively. But it should be remembered that the value of K_2/K_1 causes significant

error if they do not differ to sufficient extent. If $\log K_1$ and $\log K_2$ values differ by at least 4 pH units, then we achieve accuracy upto 0.001 for pK_1^H and pK_2^H .

Method 4 - Schwarzenbach's Graphical Method

Schwarzenbach¹² et.al. proposed this method for the determination of ionisation constants of dibasic acids by using potentiometer. It was then extended by Schwarzenbach and Ackerman¹³ for determination of stability constants of complexes.

In this method, \bar{n} and $[L]$ are first determined by plotting the values of

$$A = \frac{(\bar{n}-1)[L]}{\bar{n}} \text{ as abscisse and } B = \frac{(\bar{n}-1)}{(2-\bar{n})[L]} \text{ as ordinates}$$

All lines passing through pairs of point (A,B) should intersect when extrapolated at the point $1/K_1, K_2$.

Method 5 - Rossotti and Rossotti's Graphical Method

$$\text{The plot of } \frac{\bar{n}}{(1-\bar{n})(L)} = A \text{ against } \frac{(\bar{n}-2)[L]}{(1-\bar{n})} = B$$

is used to evaluate β_1 and β_2 . The plot is a straight line, but it deviates from straight line for higher value of $[L]$. The slope of the graph is β_2 & the intercept on Y axis is β_1

When more than two complexes coexist, graphical method¹⁴ is used to determine successive stability constants from the values of the degree of formation of the system, plot is

$$\sum_{n=0}^{\bar{n}-1} \frac{[(\bar{n}-n)/(t-\bar{n})] \beta_n [L]^{n-t}}{(t+1-\bar{n}) [L]/(t-\bar{n})}$$

Where,

\bar{n} = average number of ligands per central atom,
 t = number of ligands in the complex for which stability constant is β_t

and $[L]$ = Concentration of free ligand species.

The intercept is β_t , and the limiting slope as $[L] \rightarrow 0$ is $\beta_t + 1$

Method 6 - Least - Square Method

Consider the equation (5.71)

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

Divide equation by $\bar{n} + (\bar{n}-1)$

$$\therefore \frac{\bar{n}}{(\bar{n}-1) [L]} + K_1 + \frac{(\bar{n}-2) K_1 K_2 [L]}{\bar{n}-1} = 0$$

$$\therefore \frac{\bar{n}}{(\bar{n}-1) [L]} = \frac{(2-\bar{n}) [L]}{\bar{n}-1} \cdot K_1 K_2 - K_2 \quad \dots\dots(5.80)$$

This is an equation of a straight line. Hence the plot of

$$\frac{\bar{n}}{(n-1)[L]} \text{ vs } \frac{(2-\bar{n}) [L]}{(n-1)}$$

is a straight line. The slope of the graph is $K_1 K_2$ and intercept is $-K_1$. This values of K_1 and K_2 can be calculated if \bar{n} and pL are determined by experimental method.

Method 7 - Bjerrum's Mid-Point Method

At the mid-point of the formation curve $\bar{n}=1$,
then $K_1 K_2 [L_1]^2 = 1$ (5.81)

Taking logarithm on both sides, we get

$$\log K_1 K_2 + 2 \log L_1 = 0$$

$$\log K_1 K_2 = -2 \log L_1$$
(5.82)

The abscissa of the mid-point gives the value of β_2

Method 8 - Computer Method

All methods given above are based on graphs or on calculations. When simple systems are studied, these methods are used. But when more complex systems are considered, then handling of data becomes more difficult, and due to lack of proper judgement, there is deviation from true values. Such type of complex systems can be studied by a computer. It is a new powerful technique to handle complicated data.

Sillen¹⁵ used the computer technique for determination of stability constant of complex compounds. Now a

days, it is often used by a number of workers^{16,17}. The results obtained by this method are more accurate and hence, more useful.

5.8 SCHIFF'S BASES AND THEIR COMPLEXES

Schiff¹⁸ (1864) reported new type of compounds which are the condensation products of primary amines and active carbonyl compounds, and since then they are known as Schiff's bases. The Schiff's bases contain the azomethine group and have the general structure $RC = NR'$ where R and R' are alkyl, cyclohexyl, aryl and hydroxy aryl groups. Due to the presence of a lone pair of electron on the nitrogen atom and due to the general electron donating character of the double bond, the compounds containing azomethine group possess basic properties. However, the basic strength of the C=N group is insufficient by itself to allow the formation of stable complexes by simple coordination of the lone-pair to a metal ion therefore, the presence of a functional group with a replaceable hydrogen, e.g. -OH, -SH is necessary for the formation of stable complexes by Schiff's bases. Moreover, this group should be near enough to C=N group to permit the formation of five or six membered chelate ring around the metal ion.

The metal chelates of the Schiff's bases represent an important and interesting class of coordination compounds. Extensive work has been done on metal complexes of

Schiff's bases. The properties of the metal complexes of Schiff's bases depend on the nature of the ligand. By varying the ligands e.g. by substituting some group in the original ligand and maintaining the metal ion constant in the metal complexes, the electronic and stereochemical changes taking place can be studied. Many excellent reviews have been devoted to the coordination complexes of Schiff's bases¹⁹⁻²¹.

The transition metal complexes of some Schiff's bases are considered as models for molecules of biological interests. The probabilities of the presence of a lone pair of electron in either π or sp^2 hybridised orbital on trigonally hybridised nitrogen in the $>C=N$ groups is of main chemical and biological importance²².

The Schiff's bases as well as their metal chelates find use in various fields like organic synthesis, agriculture, dyestuff and pigment industries²³, polymer and pharmaceutical industries. The Schiff's bases have been shown to be useful as fungicides²⁴ and herbicides. The useful complexes of Schiff's bases of lead and mercury have been used for this purpose.

The Schiff's bases are among those chelating agents, which show selectivity and sensitivity towards metal ions. Hence, they find use in analytical applications²⁵. The

analytically important Schiff's bases usually contain nitrogen, oxygen and sulphur donor atoms. The Schiff's bases with sulphur donors have been found to be more selective and to form more intense coloured and stable chelates with some metal ions. This is due to the large size and lower electronegativity of the sulphur atom.

The Stability of Schiff's base complexes

Lane and Kandathil²⁶ first studied the acid dissociation constants for three types of Schiff's bases structurally similar to 8-hydroxy quinoline²⁷ in 50% (V/V) dioxane-water at 25°C and the chelate stabilities of these ligands with Cu(II), Ni(II) and Cd(II) by Calvin Bjerrum potentiometric titration technique. Martin, Janusonis and Martin²⁸ have reported the pK values for acid dissociation of several β -ketoimines and formation constants of complexes of Cu(II), Be(II), UO(II), Ni(II), Co(II), Zn(II) and Mn(II). Metal chelates with some of these Schiff's bases have been reported by using the method of Block and McIntyre²⁹.

Green and Alexander³⁰ studied the extraction of Be by N-nBu-salicylaldimine and the N-Et derivative³¹ into toluene and found favorable extraction ratios. Stronski³² has reported the radiotracer studies of the extraction and stability constants of some aromatic Schiff's base metal chelates.

The relative stabilities of 16 aldehydes and the corresponding ketone Schiff's base chelates have been reported by Nakao³³ et.al. who observed that the aldehyde Schiff's base chelates are less stable than those of corresponding ketones. Felty, Ekstron and Leussing³⁴ determined spectrophotometrically equilibrium constants describing the protonation equilibrium and the formation of binary and ternary species between Zn(II) and pyridoxal phosphate. Dissociation constants of azomethines and the stability constants of some of its transition metal chelate compounds formed by salicylaldehyde and the isomers of the nitroanilines have been studied by Movchan, Kudryavtsev and Savich³⁵. Mehta³⁶ et. al have reported the pK values ($pK_1 = 4.85$ and $pK_2 = 8.25$) for the Schiff's base derived from acetylacetone and anthranilic acid which formed complexes with Pd(II) and Zn(II). Kogan³⁷ et.al. have reported the stability constants of some chelates of Cu(II) and Co(II) with aliphatic Schiff's bases and calculated free energies, enthalpies and entropies of formation.

Mayadeo and Patel³⁸ have investigated the stabilities of Cu(II), Ni(II), Co(II), Zn(II) and Mg(II) with Schiff's bases of 3-formyl-4-hydroxybiphenyl in dioxane-water medium. Mayadeo and Eizawawy³⁹ have found out the pK values of some Schiff's bases potentiometrically in ethanol-water media. Omprakash⁴⁰ et.al studied the formation

constants of some bivalent transition metal chelates of tridentate heterocyclic Schiff's bases. Jayadevappa and Galgali⁴¹ have reported stabilities of Cu(II), Ni(II), Co(II) and Zn(II) metal complexes of salicylaldehyde and substituted salicylaldehyde amino acid Schiff's bases.

Dubey and Wazir⁴² have reported the stability constants of a number of transition metal complexes with Schiff's bases derived from salicylaldehyde and *m*-aminophenol or *m*-anisidine and established the order of stability. They have evaluated thermodynamic stabilization energy values from log K values of complexes according to the method described by George and McClure⁴³. Pathak and Joshi⁴⁴ have investigated the complexes of Zn(II) and Cd(II) with 2-hydroxy-5-chloro-acetophenone anil by potentiometric titration technique in 60% V/V dioxane-water media.

Wazir, Kachru and Girdhar⁴⁵ have found out the protonation constants of Schiff's bases derived from salicylaldehyde and *p*-aminophenol and stability constants of some transition metal complexes with these Schiff's bases. Leussing and Leach⁴⁶ have reported the rates of formation of the Schiff's bases with salicylaldehyde and EtNH₂ alaninate or β -alaninate determined in presence and absence of Zn(II). The rate constants for the reaction increase with increasing basicity of amine. Sengupta, Bera and Ghosh⁴⁷ have reported the stability constants of some bivalent transition metal

chelates of salicylidene sulphanil amide. Fahmi⁴⁸ et.al have studied acid dissociation constants of some acetoacetarylthioamides and diacetoacetarylthioamides and stability constants of their Fe(III) and Co(II) chelates. Dodwad, Patil and Datar⁴⁹ have reported the proton-ligand stability constants of some substituted salicylanils and 2-hydroxysalicylanils and found that the proton-ligand stability constants vary according to their substituents.

Khan⁵⁰ et.al have studied the characterisation and formation constants of lanthanide complexes of Schiff's base derived from sulphanilamide and salicylaldehyde. Mayadeo and Sangodkar⁵¹ have determined the stability constants of transition metal ion complexes with N-2-hydroxy-3-methoxybenzylidene-1-naphthylamine. Mayadeo and Nalgirkar⁵² have carried out potentiometric studies on metal chelates of Mg(II), Cd(II), Zn(II), Co(II), Ni(II) and Cu(II) with N-(2-hydroxy-5-bromobenzylidene)-4-methylaniline and N-(2-hydroxy-5-bromobenzylidene)-4-chloroaniline.

Sahadev, Sharma and Sindhwani⁵³ have reported potentiometric studies on some bivalent metal complexes of 2-hydroxy-1-naphthaldehyde monosemicarbazone. Mishra and Jain⁵⁴ have carried out equilibrium study of the complex formation of some lanthanide (III) ions with Schiff's base derived from some 2-aminothiazole and salicylaldehyde. Mayadeo and Kale⁵⁵ have reported potentiometric studies on

complexes of bivalent metal ions with N-(2-hydroxy-3-methoxybenzylidene)-3-aminopyridine and N-(2-hydroxy-3-methoxybenzylidene)-2-methoxy-5-acetylaminoaniline.

Sengupta and Ghosh⁵⁶ investigated the interaction of some transition metal ions with the Schiff's base ligand p-sulphonosalicylidene anil with Cu(II), Co(II), Ni(II) and Zn(II). Sengupta, Ghosh and Sanyal⁵⁷ have been reported the potentiometric investigation on the complexation of p,p-bromosulphonosalicylidene anil with Co(II), Ni(II), Cu(II) and Zn(II) at 20°C, 30°C and 40°C. Priokumar and Bannerjee⁵⁸ have described a thermodynamic study on the complexation of 2-hydroxydeoxybenzoin and 2,4-dihydroxy deoxybenzoin with Fe(III), Cu(II), Zn(II) and Cd(II).

Chandrapal^{59,60} et.al have studied and reported the formation constants of 1:1 and 1:2 binary Ln(III)-Calmagite (CLM) and 1:1:1 ternary [Ln(III)-CLM-A] Chelates (where, Ln(III)= La, Pr, Nd, Gd, Dy and Y; A = iminodiacetic acid). Dhuley and Chondhekar⁶¹ have studied thermodynamics of complex formation of rare earth metal ions with N-phenyl-2-hydroxy-5-chloroacetophenoneimine and N-naphthyl-2-hydroxy-5-chloroacetophenoneimine.

Siddiqi⁶² et.al reported the characterisation stability constants and toxicity of lanthanide complexes of Schiff's bases derived from sulphafurazole and thiophene-2-

aldehyde. Shah, Patel and Pancholi⁶³ have determined stability constants of some azomethine derivatives with Cu(II), Co(II), Ni(II) and Mn(II). Mayadeo and Gotmare⁶⁴ have reported stability constants of some bivalent metal ion chelates with Schiff's bases derived from 2,4-dihydroxy benzaldehyde. Hankare⁶⁵ et.al have determined the proton-ligand stability constant of 2, 3, 4-(carboxy phenyl) diacetylmonoxime with Cu(II), Ni(II), Zn(II), Co(II) & Mn(II).

Choudhary and Kumar⁶⁶ have reported the stability constants of w-(p-bromobenzoyl) thioacetophenone complexes with some bivalent metal ions. The potentiometric studies have been carried out on metal complexes of Mg(II), Co(II), Ni(II), Cd(II), Hg(II) and UO₂(II) with 2-methyl-3-(2'-hydroxybenzylidene)-quinazoline-(3H)-4-one and 2-methyl-3-(2'-hydroxy-5'-methoxybenzylidene)-quinazoline-(3H)-4-one by Halli et.al.

The above survey of literature revealed that no work has been reported on the complexation of the Schiff's base ligands such as 2-acetyl thiophene guanylhydrazone (ATG) & 5-bromo-2-acetyl thiophene guanylhydrazone (Br-ATG).

Therefore, the present investigation deals with the study of proton-ligand and metal-ligand stability constants of Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) with above mentioned ligands in ethanol-water medium (V/V) at temperature 25°C.

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