CHAPTER I

INTRODUCTION
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Our present study of the metal complexes is largely due to the pioneer work of Alfred Werner. The term 'complexes' or complex compounds is now employed to cover a wide range of substances comprising of not only the co-ordinate compounds of old but also chelates, ionic complexes and other similar compounds, without employing any particular bonding characteristics. These compounds may consist of complex anions or cations or both: they may also be neutral molecules.

The investigation in the subject of complex formation may be roughly said to indicate three different stages of development, namely:

(i) The work that may be styled as the early investigation making the period between the middle of the 19th century to about 1920 which was followed by a rather dormant period of about fifteen years.

(ii) The second stage in which the study of ionic complexes began with a fusing lead given by Leden, followed by

(iii) The third stage in which the study of complex formation between metallic ion and organic ligands was initiated and developed by Bjerrum. The pioneering work of this author was responsible for rationalising the solution chemistry of metal chelates and complexes.
The most of the earlier work on the subject appears to have been confined to the preparation of chelate compounds, the nature of their structure and, to some extent to the determination of their stability constants. Stability constants are needed to determine the nature of the metal complexes formed under a wide variety of conditions for many applications in diverse areas of science and industries - analytical chemistry, biological systems, complexes of metals in agriculture, corrosion and chemical cleaning detergents, electroplating, environmental problems, geoscience, membrane research, metallurgy, oceanography etc.

Bjerrum's work can be said to have stimulated the study of the other aspect of the subject. One of these important aspects is the role played by the substituents groups in the molecule of the organic compounds and the way in which they affected the physical and chemical properties of the latter. Some of the early studies in this connection are found to be mostly of qualitative nature. This comprised of the effect on water solubility of metal complexes on the introduction of hydrophilic groups -SO$_3$H, -OH, -COOH etc., They increased the water solubility of metal complexes. The introduction of hydrophobic groups such as -CH$_3$, -C$_2$H$_5$, on the other hand, decreased the water solubility of the complexes.

It was probably Berg who first examined the influence of substituents like -COOH, -Cl, -Br, -I, -S, -OH in different
positions in the oxine molecule on the selectivity of the reagent towards various metal ions in different media. He also studied the heat stability of the precipitates obtained. These results were purely of qualitative character.

The replacement of methyl group in dimethyl tellurium derivatives of B-diketones by ethyl, propyl and butyl groups increased their stability in hexane. Brass and Wirnitzer investigated the chromous complexes of salicylic acid azo dyes in which the substituents were introduced in the ortho position to azo group. From the molar ratio of the dye, water and chromium they were able to infer that the azo group may co-ordinate with the metal.

Some qualitative work on the role of substituents has been published by Perkins and Fyfe. The former author found that substitution of hydrogen in the amino group in glycine produced hardly any effect on the stability constants of the glycine complexes of the metals belonging to the IIB group. He, however, noted that an increase in the chain length of the amino-acid caused a decrease in the stability of the metal complex. The latter studied the stability constants of silver complexes of the substituted anilines and aliphatic amines. From his findings he inferred that the substituents which increased the \( \pi \)-electron density of the co-ordinating nitrogen atom were responsible for increase in the stability of the complex.
A quantitative approach to the subject was made possible when it was realised that there exists a parallelism between the metal and the hydrogen ion in reaction with a ligand L to form the complex of the type ML and HL. The reaction of the types suggested involves the donation of electron pair to the complexing ion whether it is metal or hydrogen. The extent of metal complex formation from reagent may be considered as a measure of the competition between metal ions and protons for the ligands. Hence, it is reasonable to expect a correlation between the stability constants (log $K_1$) and the acid dissociation constants $K_H$ of the ligands. Perhaps, Larsson was the first to point out that there exists a linear relationship between $pK_H$ of HL and log $K$ of ML.

Similar correlation were also reported by some workers such as Britton and Williams, and Vosburgh and Cogswell. However, the linear relationship appeared to find favour in general, with several eminent research workers in this field. Amongst these may be mentioned Bruehlman and Verhoek, Bjerrum, Calvin et al., Schwarzenbach and coworkers and Fernelius and Colobrators. The last mentioned ones have carried out intensive investigations on co-ordinating ability of diketones of the type $R-CO-CH_2-CO-R$ where the nature of the group $R$ varied systematically. They report a linear relationship between log $K$ of sodium complexes of B-diketones containing aromatic $R$ groups and
pK values of the diketones assuming the B-diketones to be largely in the enol form. They have also found that the relationship holds for many metals, the slope of the line becoming greater with more electro negative metals. In this connection, they have shown in general that the B-diketones containing two aromatic rings form more stable chelate compounds than those containing one aliphatic group. The authors have also shown that the inductive effect of substituted group is more pronounced on the complexes of comparatively more electro negative metals like copper than nickel. They observed hardly any effect on the metals with small electro negativity like Barium.

Irving and Rosotti have discussed the following relation given by Duncan.

\[
\log K = pK \left[ \frac{G^{\circ}_{ML} - G^{\circ}_{HL}}{RT} \right] + B \quad \ldots (1.1)
\]

they have derived thermodynamically a general relation between log K and pK,

\[
\log K = pK + A + B \quad \ldots (1.2)
\]

where the term B is independent of the nature of the ligand and is constant for all complexes of the given metal ion provided the composition, the solvent and the ionic strength are kept constant. For dilute aqueous solutions, the term A is determined largely by the difference in partial molar free energies \( G^{\circ}_{ML} \) and \( G^{\circ}_{HL} \) of the species ML and HL. A straight line of unit slope would indicate the term A to be constant and negligible as compared to pK. A straight line of non-unit slope would suggest that
A is linear with pK. Testing the relationship using the own data on the metal complexes of oxine and substituted oxines and those reported by other workers, they found that straight lines of unit slopes were rarely obtained. In case of substituted oxine derivatives they noted some points markedly divergent from the line of unit slope. This discrepancy has been attributed by them to steric hindrance lowering the stability of the complex. There were other small deviations also. These, they have explained by stating that while pK referred to the dissociation of the phenolic OH of the oxine, the metal in the complex co-ordinates with both -N and -O. The co-ordinating power of -N might not vary to the same extent or even in the same direction as the -O due to the structural changes in the ligand. From their findings, the authors have inferred that the linear relation will be expected in the case of the metals showing greatest tendency to form strong bonds, and hence, exhibiting the greatest differences in the relative strength of their bonds with different donor atoms.

R.J.P. Williams et al. seem to argue that the above relation of Irving and Rossotti cannot be deduced on thermodynamic groups, but they rather give stress on the nature of bonding between HL and ML. Proton is only σ-electron acceptor or donor while metal ion like Cu are π-as well as σ electron donor, acceptors. So substituents which are σ as well as π electron acceptors and substituents which are π donors but σ acceptors behave differently. They say the linear relation is only expected
to obey in the case of former type substituents. They assert that
if ligands of somewhat different characters are compared, the
general equation of Bjerrum has no general validity. They have
also made a similar discussion on the values of b, the constant
in the general equation, \( \log K = a pK + b \), and have shown that
these values change considerably from aliphatic to aromatic
ligands in the order imidodiacetic acid < phthalic acid < salicy
laldehyde < naphthaldehyde < acetylacetone < oxine.

A part of this order of b, namely salicylaldehyde < naph-
thaldehyde < acetylacetate, was explained by Calvin and Wilson
on the basis of resonance between cation and the ligands which
entitled the transfer of charge from ligand to the cation. The
authors of this paper do not accept this interpretation. They are
of the opinion that such changes are due to the ability of the
ligands to accept electron from metal through \( \pi \) bonding and also
partly due to the differences in solvation between ML and HL.
They aver that the solvation factors will be of some importance
even in a given series so that a strict linear relation between
\( pK \) and \( \log K \) cannot be expected.

Perrin from the stability constant measurements of iron-
amino acid complexes points out that if oxidation-reduction
potentials are plotted against the sum \( pK + pK \) as suggested
by Williams and coworkers, taking it as a measure of ligand
basicity, no simple relation is found. However, if only \( pK \) is
considered, a better relation is obtained with redox potentials. They advance the argument for this suggestion that if the factors governing the binding of proton and cations are similar, it seems reasonable to expect that the stability constants of metal chelates might depend on the dissociation constant of the more strongly proton binding of the two chelating groups.

Freiser and coworkers have discussed all previous approaches in which the different properties of the metal and those of the ligand have been taken into consideration are comparing them with stability constant of the complexes. They have pointed out that the correlation of stability constant with ligand basicity, although useful, has two major shortcomings. Firstly, it is difficult to justify the use of but one pK value or attempt to use a proper combination of all, since the ligand molecule has at least two basic functionalities. This difficulty is inherent in any comparison of mono basic acids $H^+$ with these of polybasic acid $H_n^+$. Second shortcoming involves the consideration of all the complex forming properties of the metal without permitting the specific evaluation of any of these. Eventually, from their findings involving the consideration of the stability constants of a wide variety of ligands, they suggested that log $K$ of metal ligand complex should be compared with log $K$ of complex of the same ligand with another similar metal. They affirm that this correlation will minimise the effect of all those properties which the metal pairs have in common and will be emphasising
those properties in which they differ, thus permitting an assessment of those differences. Because of the shortcomings pointed out they opine that the "pK stability constant" relationship is greatly restricted and only applies within a closely related series of ligands. They state that the correlation proposed by them, will be much more general in scope.

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A large number of the publications have appeared wherein they have attempted to correlate the ligand basicity with metal complex stability.

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Sun and Brewer have used metal complex stability and reagent pK values to characterise the ligand dπ - πσ bonding capacity qualitatively rather than to verify the relation.

Some of the recent important publications which have attempted to throw new ideas in the correlations of metal stability values with the reagent and metal properties are given below:

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Misno et al. have proposed a dual parameter scale.

\[-\log K = \alpha X + \beta Y + t\]  ...... (1.3)

where one parameter X is relating to electronegativity of the ion (hardness) and other parameter Y is relating to the tendency of the metal to form dative π-bond (softness). α and β are basicity parameters and Y is constant for each ligand. This relation was mainly used to assign the extent of softness with the knowledge of basicity data. In their later article they have pointed out that the above relation is useful for only rough classification.
Neiboer and McBryde compare stability constants of complexes formed by a metal ion $M$ and a ligand $L$ with those of reference metal $M_s$ and reference ligand $L_o$ they have derived the following relations,

$$\log K = B \log K_{M_sL} + (\log K - B \log K_{M_oL}) \quad \ldots \ldots (1.4)$$

$$\log K = C \log K_{M_oL_o} + (\log K - C \log K_{M_oL}) \quad \ldots \ldots (1.5)$$

They argue that there is an inherent relationship between $B$ and $C$. They have also shown how these equations under different conditions become identical to earlier published various relations.

They have also attempted to correlate the magnitude of stability constants with the properties of metal ion in their later publications. They say that, the original classification into "class a" and "class b" by Ahrland et al. have not been widely tested for indices of complex stability in solution. They have developed a new index $Q$ which is somewhat related to ZX scale (stepwise ionisation potential). This index is defined as,

$$Q = \frac{(a \Delta ZX + bX)^2}{a + b} \quad \ldots \ldots (1.6)$$

where, $\Delta$ is a parameter calculated with the acid of Slater atomic shielding constants and is intended to compensate in the case of certain elements for an effective increase in electronegativity due to small size or extra covalent bonding character. They
also argue that in the most of the metals the Q is independent of the nature of the ligand. The slope of the plot is steeper when the complex is more stable and attributed this slope to the number of donor groups. The changes in Q value (intercept of the plot) is diagnostic of the structural substituent effect. Further, they argue that the higher the Q value greater is the "class b" character. The index Q may be regarded as another way reflecting the varying degrees of ionic or covalent character in the complexes.

Steger and Corsini developed a linear correlation between the solution stability of metal oxinates and pK and pK of oxinates. They used different parameters for different donor-atom basicities. According to them, these parameters are proportional to ionic charge Z/r of the metal. They say that this correlation presents an alternative to the arguments based on the metal to ligand N bonding but fails in case of halo-substituted oxinates.

The pioneering work of Jannik Bjerrum on the study of the complex formation between a metal ion and organic ligands, particularly the one of the study of metal ammine formation in aqueous solutions is of great importance. His quantitative treatment of complex equilibria provided a sound basis for rationalising the solution chemistry of metal chelates and complexes. The concept of the stepwise formation of complexes and their mathematical treatment provided a great incentive in the exploitation
of the whole field of metal ligand equilibria in solution. While the development of the glass electrodes acted as a promoter, the impetus for the detailed researchers in this field was provided by the demands of analytical, organometallic and metallobiological chemistry since 1948. There has been an intense activity in the field of quantitative solution chemistry. The observations of Irving and Williams that the stability constants of bivalent transition metal ions increase monotonically from Mn to Cu irrespective of the nature of the ligand with a drop in stability going from Cu to Zn, was a significant contribution in the development of the study of co-ordinate complexes in general and transition metal complexes in particular.

The metal complexes of schiff base ligands have got prominent place in co-ordination chemistry over many years by the large number of publications and by several comprehensive reviews. The reasons for this sustained interest in these compounds are many, but some of the important ones among them must be their ease of preparation, their diverse properties and their use as biological models. Schiff bases are also known to posses tuberculostic, fungicidal and bacteriostatic activities.

From the review of the literature survey, the role of substituents in the chelating organic molecule and its effect on the stability of its metal complexes form a very important topic for investigation in chelate chemistry.
The study of chelate formation with reagent having more than one chelating site should be still more interesting in the investigation of the factors involved in chelate formation. In this direction, particularly no work has been carried out. Although there has been some work on metal stability constants with reagents N-salicylidene-anthranilic acid, N-salicylidene B-alanine, 2:3-dihydroxy benzoic acid, B-[3:4-dihydroxy] phenylalanine and 2:3 dihydroxybenzaldehyde which could provide such an opportunity the authors seem to have missed this very important interesting point.

In view of this the relation between metal ligand complex stability with ligand basicity and factors involved in the choice of chelation site, a systematic study on the metal ligand complexes of salicylic acid and related compound have been carried out.

Complexation equilibria of metal complexes of UO, Cu, Ni, Co and Mn with 3-aldehydosalicylic acid aniline schiff base (3ASAA) have been carried out potentiometrically. However, no proper attention has been given to determine the chelation site, in 30/70 (v/v) dioxine-water medium at 25 in a medium of 0.2M ionic strength.

Literature survey shows that a large amount of preparative work has been carried out on the reagent salicylic acid and substituted compounds of salicylic acid. And very little amount
of work has been carried out on the reagent 3ASAA schiff base.

There appears no work on any kind that has been carried out with the reagents 3 and 5-aldehydosalicylic acids, aniline schiff bases of 3 and 5-aldehydosalicylic acids and the substituted aniline schiff bases of 3 and 5-aldehydosalicylic acids, used in the present work under investigation.

Protonation (proton-ligand) and metal ligand stability constants of salicylic acid and substituted salicylic (other than hydroxy) acids have been determined by various methods such as potentiometric, polarographic, spectrophotometric, ion exchange etc., salicylic acid with metals viz., 50,52-55,58,61,65,77,87,100 51,58,80,87
Copper, 49,58,71,87, 58 54,57,62,63,72 51,60
Zinc, Nickel, 56, Magnesium, Iron, Cadmium, 54,57,59 53,60,80
Chromium, Aluminim, Beryllium, 64,71,87 80 84 71,76
Manganese, Vanadyl, Uranyl and thallium;

-nitro substituted salicylic acids with metals viz., 74,79,85,87,88,89 73,74,81,86,87,88
Copper, 74,79,85,87-90 74,79,85,87-90
Zinc, Nickel, 73 73,86,87,89 57 75,84
Cobalt, Cadmium, Manganese, Aluminium, Uranyl, 66,73
Magnesium, and Mercury;

-alkyl, amino and chloro substituted salicylic acids 87 with metals viz., copper, zinc, nickel, cobalt, manganese, iron and aluminium;

-sulfosalicylic acids with metals viz., copper, lanthanum cadmium, iron, neodymium, group IV elements and thorium;
-bromosalicylic acids with metals, uranyl, copper, nickel, zinc, cobalt and manganese are reported. -3-methoxysalicylic acid with metals Cu, Zn, Ni and Mg are also reported.

Iron(III) complexes with dihydroxybenzoic acids were investigated by Tsin-Jao Jin et al. in aqueous and aqueous-ethanol solutions. Gupta et al. have studied the complexes of Cu and Fe with 2:4-dihydroxybenzoic acid in aqueous medium potolorographically and have determined the stability constants. Gupta and Soni have determined the dissociation constant of copper complex with 2:4-dihydroxybenzoic acid at three different temperatures. They state that the plot of log K versus 1/T is linear assuming the heat of dissociation is constant in this temperature range.

The stepwise stability constants of complexes of Co, Ni, and Cu with esters of salicylic acid are determined by A.Gupta and B.S.Pannu in 50% (v/v) water-ethanol medium at ionic strengths 0.05M, 0.075M and 0.1M and at 25, 35. They have reported the stability order is Cu > Ni > Co and methyl salicylate > ethyl salicylate > phenyl salicylate. The higher values of stability constants suggest that the complexes are chelate in nature and the thermodynamic stability constants are obtained at 25.
K.J. Mandalik, C.P. Saxena and P.V. Khadikar have determined II formation constants and thermodynamic parameters of Be complexes with salicylic acid and substituted salicylic acids (5-amino, 5-chloro and 5-sulpho salicylic acids) are reported. The formation constants have been determined at 30, 35 and 40 ±0.1°C. The bonding in the complexes is discussed on the basis of IR spectra.

Pant et al. have determined stability constants of Gibbs free energies of Uranyl complexes with 2:3-, 2:6- and 2:5- dihydroxybenzoic acids at 303K and enthalpies at 293-323K temperature at the ionic strength of 0.1M. Authors have also noted that with the increase in ionic strength (μ = 0.02 to 0.2M), log K increased, decreased and decreased for the reagents 2:3-, 2:6- and 2:5- dihydroxybenzoic acids respectively.

ABOUT THE PRESENT WORK:

From the literature survey reveals that no work has been reported on protonation and metal ligand stability constants for the system of our present work under investigation would be of interest under the identical experimental conditions. The reagents selected in the system of work under investigation are: 3 and 5-aldehydosalicylic acids, aniline Schiff bases of 3 and 5-aldehydosalicylic acids, nitro-substituted anilines Schiff bases of 3 and 5-aldehydosalicylic acids and chloro-substituted anilines Schiff bases of 3 and 5-aldehydosalicylic acids (3ASA, 3ASAA, 3ASAONA, 3ASAMNA, 3ASAPNA, 3ASAOCA, 3ASAMCA, 3ASAPCA,
5ASA, 5ASAA, 5ASAONA, 5ASAMNA, 5ASAPNA, 5ASA0CA, 5ASAMCA and 5ASAPCA as shown in table III.1(a).

The protonation and metal ligand constants of these reagents with metals viz., copper(II), zinc(II), nickel(II), magnesium(II), cobalt(II) and cadmium(II) in 50% (v/v) water-ethanol medium at 15, 25, 35 and 45 (±0.1) at the ionic strength \( \mu = 0.1\text{M} \) are determined by Calvin-Bjerrum titration technique.

The knowledge of thermodynamic stabilities is essential for quantitative treatment of several analytical and biological processes for example, the knowledge of these constants is helpful for clinical purposes in the selection of suitable ligands, say the removal of unwanted exceptors from the body. 2:3-dimercaptopropanol for instance use to protect the -SH groups in enzymes from the attack of arsenical compounds used as poisonous gases during the war time. This was possible as the -SH groups of the above compound would co-ordinate strongly with arsenic rendering the later harmless.

Since the equilibrium constant \( K \) of any reaction is related to the corresponding free energy change, the corresponding entropy changes of the complex formation may be evaluated. These thermodynamic parameters are essential for a fuller understanding of many factors such as shape, size and electronic structure and stability of the complex.
Studies dealing with solution equilibria are carried out in 50% (v/v) water-ethanol medium as reagents under investigation are not soluble in aqueous media, though these reagents carry two negative charges (-COOH and -OH groups).

Chapter II comprises of a review in brief of the methods that have been employed in the present investigation. The actual study of complexes is fully depicted in Chapter III. The choice of the metals was confined only to the typical metals such as copper - a transition metal ion forming strong complexes, nickel and cobalt - transition metal ions forming moderately strong complexes, zinc and cadmium non-transition metals ions forming moderately strong complexes and magnesium a non-transition metal ion forming not very weak complexes. However, an important point which is required to be noted is that these metal ions are equally spaced in electronegativity series. Other important fact worthy of consideration is that neither the metal ions nor their complexes are in equilibrium with their other valency states under normal conditions. This latter feature is of consequence because it avoids experimental difficulties encountered in solution study of the complexes of ions.

In the III Chapter the details of the experimental technique is also given.

The calculations of the protonation (proton-ligand stability) constants are given in Chapter IV A in which the discussion
pertaining to them is also dealt with.

Chapter IV B dwells upon the manner in which the calculations of stability constants of the metal complexes are performed.

Chapter IV C deals with the thermodynamic functions such as free energy changes ($\Delta G^\circ$), enthalpy changes ($\Delta H^\circ$) and entropy changes ($\Delta S^\circ$) have been evaluated for the chelate reactions.

Attempts to establish chelation sites of reagents 3-aldehydosalicylic acid and 3-aldehydosalicylic acid-aniline schiff base are made in Chapter V. Potentiometric, spectrophotometric molaratio and conductance measurements of 1:1 and 1:2 complexes are used to establish the chelation sites. In this Chapter the relation between first stability constants ($\log K_1$) and atomic numbers, ionic-radius, electronegativity, ionisation potential of metal ions and pK values has been discussed. The effect of temperature on stability constants is also discussed considering various thermodynamic functions.

In addition to the above studies we have also synthesised some of the metal complexes of the ligands listed in Chapter III and characterised them by chemical analysis and infrared spectra.
II
IR SPECTRA OF THE CU COMPLEXES OF 3 AND 5-ALDEHYDOSALICYLIC ACIDS AND THEIR ANILINE SCHIFF BASES:

The IR spectra of Cu-complexes of 3ASA and 5ASA show a marked shift in the >C=O stretching frequency of carboxylate group from 1680 cm⁻¹ and 1662 cm⁻¹ in ligand to about 1645 cm⁻¹ and 1623 cm⁻¹ respectively in complexes.

The Cu-complexes of 3ASAA and 5ASAA also show a marked shift in >C=O stretching frequency of carboxylate group from 1723 cm⁻¹ and 1660 cm⁻¹ in ligand to about 1646 cm⁻¹ and 1605 cm⁻¹ respectively in complexes. These observations provide the evidence of metal oxygen binding in these complexes. The structure of the complexes were $\text{O}^-\text{M}$, we should observe the characteristic >C=O frequencies around 1700 cm⁻¹ in place of carboxylate frequencies observed around 1640 cm⁻¹, the absence of the bands near 1700 cm⁻¹ indicate that the carboxylate to metal bond is essentially ionic. Hence, the possible structures of Cu-complex with ligand molecules will be;

\[\text{3 ASA} \& \text{5ASA} \]

\[\text{3ASAA} \& \text{5ASAA} \]
**IR Spectra of 3ASA**

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IR Spectra of 5ASA

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High WN: 4000.0  Low WN: 401.0  Level: 60.0  Window: 2.0


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