CHAPTER I

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Historically coordination chemistry is of comparatively recent origin. Prussian blue, obtained by Diesbach in Berlin in 1704 may be considered as the earliest recorded coordination compound. The beginning of coordination chemistry is, however, usually dated from the discovery of cobaltammines by Tassert in 1793. A number of compounds e.g. red prussiate of potash, Magnus's green salts and nitroprusside were prepared in the first half of the nineteenth century. The work of Genth on composition of cobaltammines in 1847 was the beginning of a successful period of empirical work of Freseney, Blomstrand, Gibbs and particularly Jørgensen in Copenhagen until 1890.

The development of coordination chemistry was however held back by two events, (i) Kekule's theory of the tetrahedral and chain like nature of carbon compounds and (ii) emergence of classical hexagonal formula of benzene. As is well known, the foundation of coordination chemistry is connected with the name and work of Alfred Werner who in 1891 published his first epoch making paper on valence. He dealt mostly with so called substitution inert complexes, which made possible the preparation of well defined isomeric complexes. Werner's theory led to a better understanding of the structure of hundreds of complex compounds.
their stereochemistry and isomerism. It had an inherent weakness in that it postulated two different kinds of valence for inorganic substances - primary and secondary - without any justification for their existence. It was only after the development of the electronic theory of valency by Lewis, Kossel, Langmuir, Sidgwick, Fajans and others that a self consistent explanation of the ideas of primary and secondary valence could be obtained.

The nature of secondary valence was interpreted by Lewis (1) in terms of the coordinate covalent bond in which the ligand atom furnishes an electron pair which it shares with the central metal ion. Sidgwick considered that the coordination process provides an opportunity for the transition metal ion to reach the inert gas configuration or the effective atomic number of an inert gas.

Valence bond theory:

The development of coordination chemistry after the work of Werner was due to Linus Pauling who in 1931 extended the theory of valence bond. This theory, which is based on the quantum mechanical theory of directed valence due to localised electron pair and hybridization of atomic orbitals. This theory interpreted and correlated many properties of coordination complexes, such as magnetic susceptibility and stereochemistry.
According to this theory $sp^3$, $d^2sp^3$ and $dsp^2$ hybrid orbitals of the cation are employed to form coordinate covalent bonds with ligand orbitals leading to tetrahedral, octahedral and square planar stereochemistry respectively. The theory presents a quite simple picture of complexes and was widely applied by chemists (2) until the advent of the ligand field theory. It has, however, been criticized by many workers (3) as it cannot give precise quantitative interpretation and does not explain spectral properties of metal complexes.

Pauling's valence bond theory was pushed into the back ground by the development of the ligand field theory in the hands of Van Vleck (4) and his coworkers. The ligand field theory evolved out of electrostatic crystal field theory proposed in 1929 by Bethe (5).

**Crystal field theory:**

According to the theory the ligands which are generally negative ions or molecules with an unshared pair of electrons produce an electric field equivalent to that of a corresponding set of negative point charges placed around a metal ion. Orgel (6,7) made an extensive application of the theory to account for the magnetic behaviour, colour structure and stability of coordinate compounds of transition elements.
The electrical field lifts the degeneracy of the five d orbitals, splitting them into two or more sub-levels. The nature of the levels as well as their energy difference that results from splitting, depend upon the strength and symmetry of the field.

The splitting of d orbitals in the case of an octahedral complex leads to a lower energy group of three (t_{2g}) and an upper group of two (e_{g}) orbitals. This splitting pattern is reversed in a tetrahedral field. The energy difference between the two sets of levels is represented by a $\Delta$ or $10Dq$.

The electronic absorption spectrum of the complex furnishes an estimate of the energy separation between $e_g$ and $t_{2g}$ levels. The magnetic moment of a metal complex can be deduced from the distribution of electrons in the different levels. The crystal field theory offers quantitative interpretation of absorption spectra and magnetic moment of complexes (8,9).

**Ligand field theory:**

This theory is an extension of the crystal field theory which was developed by Van Vleck and coworkers. The crystal field theory takes no cognizance of directed covalent or electron pair bonds involving overlap or mixing of orbitals between the ligands and the central
atom and the interaction between the metal ion and the ligands is considered to be of purely electrostatic nature. On the other hand, in the molecular orbital theory of coordination complexes the molecular orbitals are constructed to represent the metal-ligand interaction by taking into account the overlap of ligand and metal orbitals. In both the approaches use is made of the symmetry properties of the complex. The ligand field theory seeks to bring about a compromise between the crystal field and the molecular orbital approaches. Unlike the crystal field theory, the ligand field approach takes care of the partly covalent nature of the metal-ligand bonds which helps to explain the behaviour of complexes arising from covalence. In this theory, which has the same basic approach as the crystal field theory, the splitting of the partly filled degenerate inner orbitals, e.g. d and f orbitals by ligands is considered. In an octahedral ligand field, the five degenerate d orbitals of a metal ion having a single d electron outside the closed shells are split into a set of three degenerate orbitals \( d_{xy}, d_{yz}, d_{zx} \) labelled as \( t_{2g} \) or \( d_{\epsilon} \) of lower energy and a set of the remaining two degenerate \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals called the \( e_g \) or \( d_{\gamma} \) orbitals. The energy difference between the \( t_{2g} \) and \( e_g \) sets is designated as \( \Delta \) or 10Dq with the \( t_{2g} \) levels lying 4Dq below the \( e_g \) levels 6Dq above the energy of the metal d
orbitals in the absence of the ligand field. On group theoretical notation for the octahedral group $O_h$ the splitting is described as that of a $2D$ term to give a $2T_{2g}$ term and a $2E_g$ term. This splitting pattern is said to preserve the centre of gravity of the set of energy levels.

In a tetrahedral ligand field this pattern is inverted with doubly degenerate $e_g$ levels lying lower than the triply degenerate $t_{2g}$ levels. Ligand field splitting for a tetrahedral complex has been found to be nearly half that of the octahedral splitting energy.

**Molecular orbital theory:**

The application of molecular orbital theory to metal-ligand complexes takes into account all the situations from no overlap or the electrostatic to the overlap or the covalent situation. The theory presupposes that overlap of orbitals will occur to some degree when symmetry permits. The treatment requires that certain symmetry considerations are satisfied for the overlap of metal-ligand orbitals in different types of stereochemistry of the complexes. The energy level diagram of this theory for a metal complex includes nonbonding $d$ orbitals used in $\pi^*$-bonding, and bonding and antibonding molecular orbitals formed by the consideration of metal ion and ligand orbitals of appropriate symmetry.
The ligand supplies the bonding electrons and the electrons in the metal ion d orbitals are accommodated in the non-bonding d orbitals and antibonding molecular orbitals. The molecular orbital theory can satisfactorily account for the spectral and magnetic properties of metal complexes, including those of the π type like the metal carbonyls and the metal olefines.

**Metal chelates:**

Rossoitti and Rossoitti (10) have defined a 'complex' as a species formed by the association of two or more simple species each capable of independent existence. When one of the simpler species is a metal ion, the resulting entity is known as a metal complex. The term ligand is sometimes applied to the particular atom in the molecule by means of which the molecule is attached to the central metal atom or it may be applied to the molecule as a whole. Some ligands are attached to the metal atom by more than one donor atom in such a manner as to form a heterocyclic ring. This is known as chelation. The chelates have been extensively studied in solution as well as in the solid state by many workers because of their remarkable properties and high stability. The extensive work in coordination complexes has been made possible with the help of various experimental techniques and has led to a number of empirical conclusions which have been detailed by Martell (11).
General methods of study of metal complexes:

The present work deals with the study of metal complexes in solution by potentiometry, spectrophotometry and conductometry, the salient features regarding the progress in this field are mentioned below:

Potentiometry:

Metal complex formation may be considered to be due to the displacement of a proton from the ligand causing a drop in the pH value of the solution. Irving and Rossotti (12) have given a method for calculation of stability constants of complexes by potentiometry. The general technique that is followed is due to Calvin and Bjerrum (13). Potentiometric studies of metal complexes of a large variety of polycarboxylic acids, phenols, oximes, carboxylic acids etc. have been carried out by many workers (14).

Absorption spectra:

One of the most important and characteristic features of a complex (or chelate) is its colour. Absorption spectra can, therefore, be used to distinguish between free metal ions and their complexes. Job (15) used a simple colorimetric method for determining the composition
of a complex in solution. Later he (16) found that his method was not generally applicable to systems where more than one complex was formed. Vosburgh and Cooper (17) applied Job's method to a special case in which they determined the nature of equilibria involving three chelate compounds. Many chelates of transition metal ions and rare earths with ligands having O and N atoms as donors have been investigated.

Experimental evidence for metal-ligand orbital overlap can be obtained by ESR and NMR spectra of a complex. The nuclear resonance of atom in ligands is found to be affected by unpaired electrons which may be attributed to the transfer of the electron spin density from metal orbitals into orbitals of the ligand atoms. The intensities of optical absorption bands due to d-d transition give evidence that d electrons of metal ions in the complex are not localised on the metal ion.

**Electrical conductance:**

The conducting power of electricity by means of ions in solution depends upon the concentration of the ions present in the solution and to a lesser extent upon the nature of the ions. The complex formation involves disappearance of certain ions which form the complex compound.
Werner (18) used conductivity measurements in the investigation of the nature of such complexes. Ley (19) studied amino acid chelates by this technique and molybdic and tartaric acid complexes were studied by Biswas (20). Martell (21) carried out conductometric titrations of EDTA with metal hydroxides. Some workers (22) employed Job's method for determining the composition of the complex by measuring the conductivities of the components.

Some of the other important methods used for determining the presence of chelates are:

a) Optical activity,
b) Ion exchange,
c) Oxidation potential,
d) Electro-migration studies,
e) Mossbauer spectra,
f) Magnetic measurements,
g) X-ray measurements, and
h) Polarography.

Study of metal chelates in solution:

Considerable research work has been done on the study of complexes in solution in the last four decades. The development in this field was initiated by Jannik, Bjerrum dissertation (23) published in 1941. Calvin, Bjerrum, Irving, Rossotti, Martell and Schwarzenbach have made important contributions to the rapid progress in our
understanding of metal complexes in aqueous as well as in mixed solvents.

In studying the formation of coordination complexes in solution, two kinds of stability, thermodynamic and kinetic have to be considered. The thermodynamic stability of a species is a measure of the extent to which this species will form from or be transformed into other species under certain conditions when the system has reached equilibrium. The kinetic stability of a species refers to the speed with which transformation leading to the attainment of equilibrium will occur. A number of physico-chemical methods are used for this study.

The stability of a complex in solution is governed by the nature of the central atom and the ligands. The most important characteristics of the central atom which influence the stability of the complex compound are the degree of oxidation (charge on the central ion in the case of ionic complexes) and the radius and the electronic structure. In the case of complexes with monoatomic ligands, stability is dependent on the same characteristics in the ligand as considered for the cation. The strength of binding for ligand molecules and polyatomic ions depends, in addition, on the nature of the atoms directly linked to the central atom and on the particular features of the structures of the ligand molecule or ion.
The water molecules are bound to the positive metal ion through the negative ends of water dipoles leading to high solvation of metal ions. It is evident that a fraction of the water molecules in the environment of a metal ion is directly bonded to it by the of the available electron pairs of the oxygen atom of the water molecule. This fraction can be regarded as coordinated water molecules. The number of directly coordinated water molecules can be determined from the isotopic exchange experiments (24) from NMR studies (25) and from density measurements (26,27).

As expected the number of coordinated water molecules is equal to the characteristic coordination number of the ion. Because of positive charge on a metal ion, electrons in the water molecules are displaced towards the metal which results in a loss of protons from bound water molecules. The bound molecules, therefore, lose $H^+$ more readily than the free cosolvated water molecules. A metal complex is formed by replacement of water molecules by other molecules or ions.

The complex formation is favoured by negative enthalpy and positive entropy changes. It is very difficult to predict the contribution of these terms because the solvation of the constituents of the complex also must be taken into consideration. According to Williams (28) the entropy term is usually favourable
when the ligand is anionic and is generally unfavourable in the case of neutral ligands. Enthalpy changes in complex formation are generally determined by i) temperature coefficient method and ii) microcalorimetry. The second method is more sensitive and gives more accurate results and has been used by a number of workers to determine $\Delta H$ of various complexes of transition metal ions and lanthanides (29-32).

Correlation between the basicity of the ligand and the stability of complexes:

In most cases the complex formation being a competition between metal ions and protons, it is reasonable to expect that there is some correlation between the stability constant of the complex and the acidic dissociation constant of the conjugate acid of the ligand.

Larsson (33) found a linear relationship between the corresponding constants for the complexes of Silver(I) with organic amines. Subsequently similar correlations were found in many complex systems (34-36). The ligand may affect the chelating tendency in two possible ways - (i) it may influence the basicity of the donor groups by inductive and resonance effects or/and (ii) the addition of groups on the ligand may by purely statistical (sterical) effects prevent the ligand ions or molecules from acquiring the orientation about the central metal ion most
favourable for chelation. In certain cases a linear correlation was found between the Hammett \( \sigma \) constants for the functional groups in ligands and the logarithms of the stability constants of the complexes. May and Jones (37) have applied Hammett's equation to the complexes of substituted benzoic acids. Irving and DaSilva (38) introduced a stability factor '\( S_f \)' which is a measure of the stabilization due to \( \pi \) bonding.

### Size and number of chelating rings:

The size of the chelating ring and the number of rings formed on chelation are determined by the structure of the chelating agent. Hence the stability of a chelate depends upon both the factors. Ley (13) has concluded from his work on amino acid chelates that five and six membered rings are the most stable. A large amount of evidence has accumulated since then to prove that all chelates have either five or six membered rings. Pfeiffer (39) observed that in general the five membered ring is more stable when the ring is entirely saturated but when one or more double bonds are present the six membered ring is favoured. Schwarzenbach et al. (40) have observed that there is a decrease in chelate stability with the increase in ring size.
Effect of metal ion:

The stability order of metal complexes of transition metal ions is found by Irving and Williams (41,42) by comparing the ionic radii and second ionization potentials of the metal ions, because it is valid for most nitrogen and oxygen donor ligands. This order was rationalized as

\[ \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}. \]

Applications of coordination complexes:

Coordination complexes cover a wide range of applications in various fields of human interests. Some of the important ones are as follows:

i) Separation and purifications of lanthanides by making use of chelating agents like EDTA, NTA (43,44,45).

ii) Anion exchange method for the recovery of uranium from its low grade ores for its separation from many other metals by complexing it with \( \text{SO}_4^{2-} \) ions (46,47).

iii) Extensive analytical applications with techniques like titrimetry, spectrophotometry, polarography, chromatography and electrophoresis.

iv) Water softening, in activation of metal ions, precipitation analysis, repression of catalytic
reaction and a great variety of specific analytical tests both qualitative and quantitative.

v) Use of unnatural chelating agents in biological systems:

a) Destruction of organism by chelation of essential metals - bactericidal and fungicidal action.
b) Inhibition of certain metals and metal enzymes for the purpose of studying functions of metals and enzymes in biological media.
c) Removal of undesirable and harmful metals from living organism.

Sulphonic acids as chelating agents:

Dihydroxy and amino hydroxy phenols or naphthols act as good chelating agents. Sulphonates of these ligands have been used as chelate forming agents because of the increased solubility of these derivatives in water than the parent ligands. The metal complexes of dihydroxy naphthols, 8-amino-1-naphthol sulphonates, catechols, 8-hydroxy-quinolines, nitroso-naphthols etc. have been reported by a number of workers(14).

Banerji and coworkers studied the Fe(III) ion complexes of 8-hydroxy-quinoline-7-sulphonic acid by spectrophotometric technique (48), and metal chelates of uranium and thorium with 1:8-dihydroxy-naphthalene-
-3:6-disulphonic acid by potentiometric technique has been carried out by Banerjee et al. (49). Martell et al. (50) have examined the interactions of uranyl ion with Tiron (pyrocatechol-3:5-disulphonic acid) by potentiometric and spectrophotometric techniques in the pH range 2.0-11.0. McBryde (51) also has studied the iron(III)-Tiron system spectrophotometrically and proved the formation of 1:1, 1:2 and 1:3 complexes. The study of Th(IV), UO₂(II), Ti(IV) chelates of 1,8-dihydroxy-naphthalene-3,6-disulphonic acid at 0.1M (NaClO₄) (52-54) and with Be²⁺, Cu²⁺, UO₂²⁺ have been made potentiometrically at 0.1M (KNO₃) (55-57). The stability constants of the metal complexes of UO₂(II), Cu(II), Ti(IV) and Fe(III) chelates of 4,5-dihydroxy benzene-1:3-disulphonic acid (Tiron) have been determined spectrophotometrically (14).

Vartak and Jose (58) have studied the stability constants of 8-amino-1-naphthol and its different sulphonic acid derivatives at 30°C and at 0.1 M ionic strength by potentiometric technique. The stability constants of complexes of Co²⁺, Cu²⁺, Mn²⁺, Fe²⁺, Ni²⁺ and Zn²⁺ with 8-amino-1-naphthol-5,7-disulphonic acid have been determined at zero ionic strength medium potentiometrically (14).

Recently Bajue and others (59) have reported the acid dissociation constant of potassium salt of 1-hydroxy-2-nitroso-naphthalene-4-sulphonate in aqueous medium.
The formation of Ni(II) chelates of 2-nitroso-1-naphthol-4,8-disulphonic acid was a subject of investigation by Makitie and others (60).

Sodium salt of 1-nitroso-2-hydroxy-3,6-disulphonate (nitroso-R-salt) has been used as a chelating agent and also a colorimetric reagent for the estimation of Co(II), Ni(II), Cu(II), Fe(III) and Pd(II). Mandel and Dey (61) while studying the complexes of nitroso-R-salt with Ti(IV), Zr(IV) and Hf(IV) reported the thermodynamic formation constants for the above metal chelates. Patel et al. (62) determined pK values of -SO\(_3\)H group of 7-nitro-8-quinolinol-5-sulphonic acid by conductometric technique.

The transition metals, lanthanides and uranyl complexes of 5-sulphosalicylic acids have been studied by Jahagirdar and Khanolkar (63), Kanekar (64), and Bartuszek (65), and Banks and Singh (66).

Aim of the present work:

The stability constants of the metal complexes with substituted sulphonic acids have been determined by a number of workers. However, a detailed study of complexes under identical set of experimental conditions which would cover manifold aspect of complexation is still lacking. The present work is, therefore, undertaken to make a systematic study of the chelates in aqueous
as well as in different dioxane-water medium. A systematic study of stability constants of complexes of dihydroxy and aminonaphthol sulphonic acids with transitional metal ions, Fe$^{3+}$, Cr$^{3+}$, and Al$^{3+}$, uranyl, vanadyl, and lanthanide ions by potentiometric technique at 30°C in aqueous medium at 0.1 M ionic strength has been made in this investigation. Some of the systems have also been investigated spectrophotometrically and the values obtained by the two techniques are compared.

The experimental data of pK or log K values of various systems are used (i) to understand the effect of substituting groups on the dissociation of $\text{-NH}_3^+$ and $\text{-OH}$ groups of the 8A-1N sulphonic acid, (ii) to check the validity of Hammett's equation for proton-ligand and metal ligand systems and (iii) to test the relation $\log K = apk + b$ for substituted sulphonic acid complexes of 8-amino-1-naphthol.

To understand the role played by the solvent medium on the stability constants of the metal complexes, log K values for some systems were evaluated in dioxane-water mixtures of different compositions. The experimental values are utilised to examine the relation between pK or log K vs $1/D$ and mole fraction of dioxane. The validity of the Born equation is also examined. The effective ionic radius of some sulphonic acids are calculated with the help of this equation.
The effect of the ionic strength measurements on some equilibria of complexes is studied in aqueous and in dioxane-water media. The values of $pK$ and $\log K$ at different ionic strengths are utilised to estimate the thermodynamic stability constants at zero ionic strength and to know the exact nature of complexation equilibria. The variation of $pK$ and $\log K$ with dielectric constant of the solvent medium is examined and the role of dioxane in these complex equilibria is discussed. The distance of closest approach between the metal ion and the ligand is calculated in aqueous and different dioxane-water mixtures.
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