## 1.1 Introduction

Spectrophotometry is an instrumental method of analysis widely adopted because of the high precision sensitivity, and availability of the instruments used. Spectrophotometric methods enable nearly all the elements to be determined over a wide range of concentration in most materials. They are of particular importance in trace analysis, testing of high purity materials, environmental studies and biochemistry. The basis of spectrophotometric methods is the simple relationship between the absorption of radiation by a solution and the concentration of the coloured species in that solution. This relationship is governed by Beer's law. In order to determine species spectrophotometrically it is usually converted into a coloured compounds. The colour of the substance itself is utilized much less than often.

However, spectrophotometry is one of the most useful tools for elucidating the complex ions in solution and for determining their formation constants. The power of technique lies in the fact that quantitative absorption measurements can be performed without fear of disturbing the equilibria under consideration. Although most spectrophotometric studies of complexes involve systems in which one of the reactants or the products absorbs, thus condition is not necessary provided that one of the components can be caused to participate in a complete equilibrium that does produce an absorbing species.

There is a close relation between the absorption spectrum of a substance and its electronic structure. A molecule (or ion) exhibits absorption in the visible or ultraviolet range, when radiation (photons) causes an electronic transition, of some of the valency electrons from the

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ground state to an exited state. Irradiation causes variation in the electronic energy of molecules containing one or more chromophoric groups i.e; groups with unsaturated linkages. Some examples of the common chromophoric groups are: C=O, -N=N-, C=N-NH-, C=N, C≡N and C=S. Two or more chromophoric groups in the molecule often enhance one another's effect, to deepen the colour by displacing the absorption maximum ( $\lambda_{max}$) toward longer wavelength.

As the pH is increased, spectrophotometric reagents ionize and their electronic structures change, leading mostly to a shift in the absorption maximum. Ionization causes polarization of the chromophoric system.

The term ionization constants refers to those constants which are used the strength of acids and bases. In heterocyclic chemistry, the study of such constants has many useful applications, e.g; they can be used to investigate the point of equilibrium in tautomeric substances and to help in establishing the structure of newly isolated substances.

The determination of pK value is of great importance in spectral studies of many organic compounds. As different ionic species have different spectra. Little reliable or useful spectrophotometry can be carried out before ionization constants have been determined.

Various methods are known for determining the ionization constant of chemical compounds, the most important of which are the potentiometric, polarographic and spectrophotometric methods. Raman spectroscopy and nuclear magnetic resonance were also used for determining low pK values, Viz, strong acids and weak bases. The determination of ionization constants by conductometry is also known to be

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an accurate method but not very versatile for measuring second or third ionization constant in polyionic substances.

Measuring the increase in solubility at various pH values may give approximate ionization constants in cases where potentiometry, polarography, spectrophotometry and conductometry can be used, e.g; highly insoluble substances with no useful spectra.

Some organic compounds, especially those containing ionizable center directly attached to the $\pi$-system of the molecule undergo a remarkable colour changes through their ionization process. Mostly, these compounds can be used as acid-base indicators. The importance of such compounds increases if they have chromophoric properties, thus, acting as metal indicators.

The chromophoric reagents are capable of forming complexes with number of cations, the formation of these complexes is being accompanied by a change in colour at a certain pH value. Such chelates are characterized by their high stability. A large number of such organic reagents giving visible colour reaction with metal ions are known to analytical chemists. Their investigation has directed towards their application in colorimetric analysis specially for substances in small amounts or traces, where application of other conventional methods of analysis is impossible. The utility of such compounds is hence most frequently important from several points, namely, high selectivity of reaction, high solubility of the coloured complex, exact stoichiometric composition, sensitivity of colour reaction and stability of the coloured complex.

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A good metal indicator must meet a number of requirements:

a) The absorption maximum of its chelate must be sufficiently far from that of the free indicator at the same pH value.

b) Both the indicator and its chelates must be sufficiently soluble in water or any other suitable solvent.

c) The reaction with cations must be sensitive and practice instantaneous.

d) The stability of the metal indicator complexes must meet the requirements of the purpose of use.

If it is to be used as a metallochromic indicator, the apparent stability constant of the metal indicator complex must be lower by at least one order of magnitude than that of the metal-titrant complexes in the pH range suitable for a given determination. If it is to be used as a chromophoric indicator, that is, as a spectrophotometric reagent, its complex with metal ions should be extremely stable and different in colour from the reagent at the same pH value.

From the structural point of view, chromophoric reagents must posses a grouping capable of chelate formation joined directly to the resonant system of a ligand. The free electron pairs of suitable disposed oxygen and nitrogen ligand atoms in hydroxy, azo, azomethine, Schiff bases, for example will coordinate with the metal ion, forming stable five or six membered chelate rings.

The mode in which these electrons originally participated in the electron system of the ligand, corresponding to the light absorption at a particular wavelength, is altered by the process of chelate formation and

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as a result the absorption maximum is displaced to a different wavelength. Experiments show that the majority of metal indicators also behave as acid-base indicators. This is due to the fact that changes in colour will also accompany the dissociation of protons.

Moreover, it should be stressed that the colour change included by cations lies practically within the limits which can be reached by changes in pH. From the point of view of the electronic configuration, the effects of dissociation or protonation and chelation are almost the same.

The function of a metal indicators follows from a just position of its properties as a chelating agent and as an acid-base indicators. The competition between protons and metal ions for the complex forming grouping of the indicator will lead, within certain pH limits, to an interference with the normal course of the acido-basic changes. The cation will, to an extant, depends on the factors normally affecting chelation, Viz, ionic radius , electron affinity ($E_A$) and the prevalent pH, induce in the ligand an electronic configuration capable of existence at this pH in absence of metal ion. This leads to a shift in the absorption maximum toward the position characteristic of that particular form of the unchelated ligand whose electronic structure resembles closely that of the chelate.

From the above consideration, it follows that the necessary attributed of a metal indicator is essentially dependent on a suitable balance of three structural features of the molecule, Viz, the electronic system of the ligand, the acid-base properties and the complex forming grouping. The resonant system of the organic molecule is in fact the source of colour and as such it is present in practically every true organic ligand.

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The presence of acid-base properties in metal indicators is by no means fortuitous, but is indeed, one of the necessary attributes of such compounds. The only point of importance is its ability to undergo marked change in colour with progressive change in acidity. Thus from a knowledge of the pH indicator properties of a given compound, it is possible to predict probable scope of its metallochromic or its chromophoric properties.

The chelate forming system of the known metal indicators as a rule involves two separate groups placed so as to allow the formation of a chelate ring, at least one of these groups being directly linked to the conjugated system of the molecule. In most of the indicators in current use, this is an (OH) group which is also responsible for the acid-base properties of such a ligand and hence it constituents a common factor in both acid-base and chelate forming properties.

Vibrational spectroscopy is also a very helpful technique in the study of metal complexes. It has been concerned with the determination of molecular symmetry, but many applications of this method have as their objectives only the identification of molecule or a functional group. In such fingerprinting applications the frequency, shape and intensity of a band are all useful characteristics. Vibrational spectra of metal complexes can be classified into ligand vibrations which occur in the high frequency region (4000-600 $cm^{-1}$) and metal-ligand vibrations which appear in the low frequency region (blew 600 $cm^{-1}$). The former provides information about the effect of coordination on the electronic structure of the ligand while the latter provides direct information about the structure of the coordination sphere and the nature of the metal-ligand bond. Since the

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main interest of coordination chemistry is focused on the coordination bond, the latter has attracted particular interest of inorganic chemists.

The ir, $^1$H-nmr, epr and the uv- visible spectroscopy as well as the conductometric, potentiometric and polarographic techniques, all were employed successfully in our studies in order to determine the nature of newly formed metal complexes, as explained in the next chapters.

## 1.2. Literature Survey on Microdetermination of Lanthanide and Transition Metal Ions:

Many chemical, magnetic and spectroscopic data on the electronic structure of the lanthanide in the atomic and ionic states have been reported(1-3). It is firmly established that the unusual change in the properties within the lanthanide family is due to the order of filling of the electron shell. Because of the nature of the wave function of the lanthanide, the filling of the *4f* shells is energetically more advantageous than the filling of the outer *5d* and *6p* shells. Only for a few elements a single electron is bound more strongly in the *5d* shell than in the *4f* shell. The extraordinary similarity in chemical properties of lanthanide is attributed to the filling of the inner *4f* shell.

In view of this similarity, isolation of the pure elements and their individual characterization and determination require considerable efforts. Methods used for determining these elements are discussed below.

### 1.2.1. Complexometric titration:

EDTA is the most widely used reagent for complexometric titration of lanthanide and transition metals. The determination of these metal ions with EDTA is usually carried out in weakly acidic media, but

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occasionally in weakly alkaline media under certain conditions. The pH may vary between 4.00 and 10.00, and the optimum condition are selected for accurate detection of the equivalent point and to prevent the interferences by many metals. However, Zr, Hf, Bi, Fe, Cr, Sc, Hg ions affect the analysis under all conditions. In practice, the most convenient pH is 4.00 and 6. 00. Ca, Mg and Mn do not interfere. The effect of Al is eliminated by the addition of sulfosalicylic acid, and the effect of U, Fe, Co, Ni, Zn, Cd, Hg, and Pb is masked by dithiocarbamate and sulfosalicylic acid(4).

Lanthanide elements can be determined in alkaline solutions, only if they are present in a pure state. According to few published methods, the analysis is carried out in the presence of citric or tartaric acid(5,6) which prevent hydrolysis of the lanthanide ions. Since the reaction with EDTA under these conditions is slow especially near the equivalent point, it is recommended to carry out the titration on hot solutions or to measure the excess EDTA by back-titration with standard solution of Zn or Cu salts. Microgram levels of lanthanide can be accurately measured with an error of ± 2%(4-7).

### 1.2.2. Spectrophotometric methods:

The absorption spectra of lanthanide metal ions are very specific for each element, and reflect electron transition of the *4f* and *5d* shells. They consist of fairly narrow bands and lines whose intensities are usually characterized by molar extension coefficient between 0.1-1.0, which determine the range over which these elements can be determined in their mixtures.

The absorption spectra of lanthanide and transition metal ions in solutions have been extensively studied(8-11). From a practical point of view, the most important investigations are those carried out in solutions of chloride(12-14) and perchlorate(15). The absence of intense lines in the visible region is a characteristic feature of these spectra. The most intense line, with Ɛ>10, are exhibited only by Pr and Nd, and the spectra of the other elements have only a few weak lines and bands.

Many reagents, however have been used for the determination of lanthanide and transition metal ions in solutions. The chromogenic reagent reacts with these metal ions to give coloured products which can be colorimetrically or spectrophotometrically monitored.

### 1.2.3. Polarographic methods:

**Bruckel**(16)investigated the reduction of 0.01 M solutions of $Sc^{3+}$,$Y^{3+}$ and the rare earth sulphates in the absence of a supporting electrolyte. They obtained a double step for each element and concluded that the reduction proceeded firstly to the bivalent state and finally to the metallic state. The results obtained by these workers are summarized in the following table.

| Element | Reduction Potential in Volts Vs. S.C.E | |
|---|---|---|
| | First step | Second step |
| $La^{3+}$ | -1.94 | -2.04 |
| $Sm^{3+}$ | -1.72 | -2.01 |
| $Eu^{3+}$ | -0.71 | -2.51 |
| $Gd^{3+}$ | -1.81 | -1.96 |

**Laitinen and Taebel**(17) have further investigated the reduction of Europium in the development of a polarographic method for determining

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the concentration of this element in rare-earth mixtures; using a 0.1 M ammonium chloride base solution. They obtained a well-defined step with an $E_{1/2}$ of -0.67 V vs. S.C.E. due to the reduction of the trivalent ions to the divalent state.

Herman(18) obtained three steps at approximately - o.2 V, -0.4 V and - -1.1 V vs S.C.E. for the reduction of auric chloride from a 2 M potassium hydroxide base electrolyte. Since the auric hydroxide complex slowly decomposes to the aurous complex, standing or heating the above solution results in the step at -0.4 V decreasing in height whilst that at -1.1 V increases in height. Linhart(19)used a sodium hydroxide base electrolyte for the determination of traces of gold in metallic silver samples. The material is dissolved in aqua regia and the nitric acid then expelled by evaporation. The resulting solution is made alkaline with sodium hydroxide and the polarogram recorded after adding 1 ml of 0.5% gelatin per 20 ml of solution. The height of the step at - 0.4 V vs. S.C.E. is measured and the gold content obtained by referring it to a suitable calibration graph.

Herman(18) observed two steps for auric ions from a potassium cyanide base electrolyte; the first at zero applied voltage being due to the reduction to the aurous state and the second at -1.4 V vs. S.C.E. resulting from the reduction of aurous complex ions to the metallic state. The second step is very suitable for analytical work and Herman uses it in a procedure for determining the gold content of ores. A solution of the material is treatment with an excess of potassium iodide to reduce the gold to the aurous condition. Excess of sodium sulphite is then added to reduce free iodine, followed by potassium cyanide and potassium hydroxide to make the final solution 0.1 M in KCN and 2 M in KOH. After

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filtration, the aurous step is recorded and evaluated. It is important to add the potassium cyanide before the potassium hydroxide in this procedure, because although the cyanide complex is more stable than the hydroxide complex, the rate of conversion of the latter into the former complex is very slow.

The polarographic method was used extensively for the determination of copper in a wide variety of materials because of the well-defined steps obtained from many different base electrolytes. Methods are now established for its determination in aluminium, magnesium, zinc, lead and tin base alloys, steels,ores, plant materials, etc. For the determination of very small quantities of copper in animal tissues an indirect method using salicylaldoxime is recommended by Carruthers(20). Copper is precipitated by this reagent which also reduces from a phosphate buffer of pH=5.4 giving a quantitative step with a half-wave potential of -0.98 V vs. S.C.E. Therefore, the copper concentration is established by precipitating it with salicylaldoxime and determining polarographically the amount of this reagent used up in the process. There is no interference in the method from iron, sodium, potassium, calcium and magnesium but zinc interferes very seriously.

Polarography has been extensively used in the study of complexed metal ions which are reversibly, electroreduced at the dropping mercury electrode(21-23). If the metal ion forms only one complex over a considerable range of ligand concentration, it is possible to determine from the plot of the half-wave potential against the logarithm of the ligand concentration, the number of ligands bound to the metal ion, and by the shift in the half wave potential from that of the simple ion, the dissociation constant(24) can be also determined.

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**Kapoor et. al**(25), studied the complexation of some transition metal and N,N-dihydroxyethylglycine employing the technique of d.c. polarography, cyclic voltametry and differential pulse polarography. Conditions were standardized in which metal ions gave a distinct d.p. polarographic peak. Estimation of metal ions in low concentration has been made possible by the d.p. technique.

**Khan et.al;**(26) investigated the stability constants and thermodynamic parameters of $pr^{3+}$ and $Nd^{3+}$ in the presence of increasing concentration of complex forming agent viz hydroxylamine, hydrazine and phenyl hydrazine polarographically under ionic strength $\mu=1.0$ adjusted with potassium chloride. The values of the kinetic parameters $\alpha n_a$ and $k^{o}_{f,h}$ have been calculated as a function of the ligand concentration. The polarographic wave was precisely proportional to the concentration of metal ions. Hence the straight line is useful as a calibration curve in quantitative analysis of these two metal ions.

The composition, stability constant and thermodynamics parameters of polarographic reduction of $Ce^{3+}$ complexes with crotonic, cinnamic, itaconic and citraconic acids was investigated(27) at pH=2.75 ±0.02 under fixed ionic strength at $\mu=1.0$ adjusted with KCl. **Lingane** treatment of the data revealed the formation of 1:1 complexes of $Ce^{3+}$ with all the four ligands. The values of kinetic parameters, transfer coefficient ($\alpha$) and formal rate constant ($K^{o}_{f,h}$) have been determined.

## 1-3 Literature Survey on Schiff Bases Complexes:

Schiff bases are azomethines characterized by the presence of diatomic grouping CH=N. They act as multidentate ligands with metal ions, forming coloured chelates. These chelates are then used in selective

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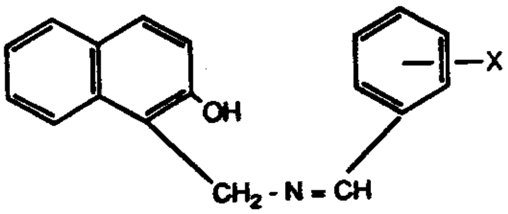
and sensitive determinations of the metals. The ligands may be coordinated to the metal through the nitrogen atoms either alone or in combination with some other electronegative atom such as oxygen or sulpher. In the following survey, the Schiff bases which have been more extensively studied from the analytical point of view are usually taken into consideration.

The synthesis and characterization of $Cu^{2+}$ and $Ni^{2+}$ complexes with the following tridentate dibasic Schiff bases are described(28)



Where X=H (1) X=3-$OCH_3$ (3)
X=5-$CH_3$ (2) X=5,6-$C_6H_4$ (4)

The structure of the complexes have been discussed on the basis of elemental analysis, electronic spectral data and infrared spectroscopy.

The chelate formation of $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ ions with tridentate vanillidene anthranilic acid had been investigated(29). The chelates formed have 1:1 stoichiometry ($M^{n+}$:L). The complexes have been isolated in the solid state also. They have been characterized on the basis of analytical and IR data. The relative thermal stability for the vanillidene anthranilic acid metal complexes followed the order $Co^{2+}$ $=Ni^{2+}>Zn^{2+}>Cu^{2+}$.

Complexation behaviour of vanillin-anthranilate (Van-An) towards $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Fe^{3+}$ has been studied(30). The resulting complexes are characterized on the basis of analytical, infrared

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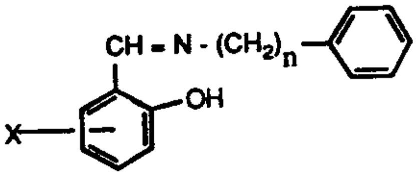
and electronic spectral, and magnetic susceptibility data. The Schiff bases coordinates through O and N atoms acting as a bidentate monobasic ligand. The subnormal magnetic moments obtained (at room temperature) in case of $Co^{2+}$, $Ni^{2+}$ and $Mn^{2+}$ complexes had been indicated due to oxygen bridged dimeric structure in the light of ir spectral data.

The chelates of zinc chloride with the following series of Schiff bases were studied$^{(31)}$. The conductometric study revealed that the formation of complexes have the stoichiometric ratio (1:1).



| | | | | | |
|---|---|---|---|---|---|
| $B_1$; | X=H , | n=1 | $B_5$; | X=5-$NO_2$ , | n=1 |
| $B_2$; | X=H , | n=2 | $B_6$; | X=5-$NO_2$ , | n=2 |
| $B_3$; | X=3-$OCH_3$ , | n=1 | $B_7$; | X=3-$NO_2$ , | n=1 |
| $B_4$; | X=3-$OCH_3$ , | n=2 | $B_8$; | X=3-$NO_2$ , | n=2 |

The structure of the ligands and the solid complexes was studied by $^1H$ nmr and ir spectroscopy which showed that chelate formation takes place through the C=N and neighbouring OH group and lead to proton displacement.

The complexes of $Ce^{3+}$, $Sm^{3+}$, $Gd^{3+}$, $Dy^{3+}$, $Co^{2+}$ and $Cr^{3+}$ with tridentate Schiff base derived from the condensation of o- aminophenol and β-naphthylglyoxal have been prepared and studied by uv-visible and infrared spectroscopy$^{(32)}$. The stoichiometry of the complexes is established by spectrophotometric methods of analysis and elemental

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analysis. The binding of the functional groups of the ligand to metal on complexation have been confirmed by infrared spectral study.

Synthesis and characterization of $Mn^{2+}$, $Co^{2+}$ $Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ complexes with the Schiff base salicylaldiminobiacetyl monohydrazone (SALBAMH) were described(33). The complexes isolated had been characterized by elemental analysis, molar conductance values, molecular weights and spectroscopic (uv-visible, ir and magnetic moment) data. Coordination occurs through the azomethine group and the phenolic oxygen after deprotonation of the OH group, ortho to the azomethine linkage.

Uranyl complexes of Schiff bases obtained by condensing substituted salicylaldehydes with aromatic amines, e.g. 2-aminopyridine, aniline and nitroaniline, have been isolated and characterized(34). The complexes had the formula $ML_2$ and $M(LH)_2(NO_3)_2$ where $M=UO_2$, and L and LH=Schiff base. The magnetic susceptibility values of all the ligands and their complexes have been compared with the computed ones, obtained by adding the experimental molar susceptibilities of the components, assuming strick additivity. The percentage deviations between the observed and the computed values clearly showed that they are outside the experimental error, and therefore are significant. These deviations have been discussed in the light of Van-Vleck's equation(35) for the molar susceptibility of polyatomic molecule.

Neutral copper (II) complexes of Schiff bases derived from substituted salicylaldehyde and 2- aminopyridene methyl derivatives had been synthesized by an electrochemical procedure(36). The crystal and molecular structure of bis {N-(2-[3-methyl pyridyl])-5-methoxy

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salicylideneiminato} copper (II) and bis {N-(6- methylpyridyl)}-salicylideneiminato} copper (II) had been determined by X-ray diffraction. In both structures, the metals adopt square-planar coordination geometries and the pyridyl nitrogen atoms are not coordinated. The electronic and ir spectra of the complex were discussed and related to the structure.

The synthesis of binuclear complexes obtained by the reaction of aromatic diamines with the ternary complexes of Cu (II) with bis (2-pyridyl) amine (dpa) as primary ligand and salicylaldehyde or 2-hydroxy naphthaldehyde as secondary ligand have been reported(37). The complexes have been characterized by elemental analysis, conductance, electronic and spectral studies. Magnetic measurements indicate antiferromagnetic exchange between two copper (II) centers. Epr spectra exhibited $\Delta M_s = 2$, transition, supporting the antiferromagnetic coupling.

**Roy** et.al;(38) studied the reaction of N ( o-vanillidene) L-alanine (oVALa $H_2$), N-(salicylidene) L-valine (oVVaL $H_2$), N-(o-vanillidene) L-tyrosine (oVTyr $H_3$) and N-(salicylidene) L-glutamic acid (SGlu $H_3$) with $La^{3+}$ $Pr^{3+}$, $Nd^{3+}$ and $Sm^{3+}$ to yield new chiral complexes. Their dominant conformers were determined from c.d. spectra supported by $^1H$-nmr data, except for the L-glutamic acid derived complexes which were insoluble.

**Prabhu** et.al(39); studied the magnetic susceptibilities of $UO_2^{2+}$ complexes with salicylanil and some closely related Schiff base ligands by the **Gouy** method. The susceptibility values were also obtained. The two sets of values were compared and the deviation from ideal behaviour had been explained on the basis of **Van-Vleck's** equation (35).The deviation (% $\Delta Xm$) had also been used to explain the symmetry of the complex molecule.

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Further attempt has been made to correlate pK values of the complexes with deviation from ideal behaviour. Validity of Ikenmeyer's relation(40) had been tested and it was found that the relation was obeyed by most of the complexes.

Complexes of $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Zn^{2+}$ and $Pt^{2+}$ with 3-and 5-substituted salicyladehyde benzylhydrazones (XSBH, X= H, 3-$NO_2$,3-$OCH_3$, 5-Br, 5-$CH_3$ or 5-$NO_2$) were prepared(41) and characterized by elemental analysis, conductance measurements, magnetic moments (300-78k) and spectral studies. On the basis of these studies, the following structures were suggested: distorted octahedral for Mn $(XSBH)_2$, dimeric, low-spin, five-coordinate for Ni (XSBH)Cl. $2H_2O$, dimeric, high-spin, five-coordinate for Co (XSBH) Cl. $2H_2O$, dimeric, four-coordinate for Zn (XSBH) and a square-planar structure for **M** (XSBH) Cl. $H_2O$ (M= $Cu^{2+}$ or $Pt^{2+}$). The polycrystalline esr spectra of $Cu^{2+}$ complexes were isotropic indicating a $d_{x^2-y^2}$ group state in square-planer stereochemistry. All the metal (II) complexes were screened for their antitumor activity against the $P_{388}$ lymphocytic Leukaemia test system in mice and were found to possess no significant activity at the dosages used.

Salicylaldehyde (N-o-hydroxybenzalidene) tyrosyl hydrazone (sal TH) had been found to form complexes of the types [M(sal TH) $Cl_2$ $(H_2O)]$ $2H_2O$ and M (sal $T\bar{H}$ .$3H_2O$). $H_2O$, where M= $La^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$ and $Dy^{3+}$ (42). The complexes had been characterized by elemental analysis, molar conductance, magnetic susceptibility, infrared, electronic and nmr spectroscopy. The nephelauxetic ratio (β'), covalency (σ) and the bonding parameter ($b^{1/2}$) had been calculated for the neodymium complexes. Infrared spectral studies showed that the sal HT acts as a neutral bidentate ligand in the adduct complexes and as a tribasic

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pentadentate one in the neutral complexes. A coordination number six had been proposed around the metal ion in all the complexes.

Polymeric complexes prepared⁽⁴³⁾ by solid-solution reactions, from 2-hydroxy-1-naphthaldehyde oxaldihydrazone (HNODH) and 2-hydroxy-1-naphthaldehyde malondihydrazone (HNMDH), had the empirical composition M(L-2H) $nH_2O$ where M = $Fe^{3+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Hg^{2+}$; L = HNODH, HNMDH and n = 0,1, 2. The complexes which are intensely coloured and insoluble in common organic solvents, were characterized by elemental analysis, magnetic susceptibility, electronic and ir spectral data. The absence of anions indicates that the ligands which bind the metal ions from the hydroxyl and the imino groups had been deprotonated.

Neutral complexes of the type M(SA) $nH_2O$, where M = $VO^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ or $Zn^{2+}$; SA = dianion of salicylaldazine; n = 1 for $VO^{2+}$ and $Zn^{2+}$, and 2 for other metal ions, had been prepared⁽⁴⁴⁾. The complexes were non-electrolytes as evidenced from low values of their molar conductance (10-15 $\Omega^{-1}$ $cm^2$ $mol^{-1}$) in DMF solutions. The magnetic moment values and electronic spectral data suggested that the $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$ complexes were outer-orbital octahedral while $Cu^{2+}$ complex was distorted octahedral. Infrared spectral studies indicated that $SA^{2-}$ behaves as a tetradentate ligand bonding through the two azomethine nitrogen and both the phenolic oxygen. TGA and ir studies showed that the water molecule (δ) are coordinated in all the complexes except the $Zn^{2+}$ complex where it was present out of the sphere.

**Gowda et.al**⁽⁴⁵⁾; reported the reaction of Au (III) with propericiazine (ppc), 2-cyano-10-[3-(4-hydroxy-1-piperidinyl) propyl] pheno- thiazine as a

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sensitive reagent and a method for the spectrophotometric determination of microamounts of Au (III) in solution had been proposed. The method offered the advantage of simplicity, selectivity, good sensitivity, rapidity, and a wide range of determination without the need for extraction or heating.

Lanthanide chloride complexes with pyridinaldazine (PAA) and pyrrolaldazine (Py AA-$H_2$): [Ln (L) $Cl_2$ $(H_2O)_n$] Cl. $mH_2O$, where Ln = $Ce^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Yb^{3+}$; L = PAA, PyAA-$H_2$; n = 2,4; m = 0,1,2,3,5 had been prepared(46) by the reaction of the corresponding lanthanide with PAA or Py AA-$H_2$ ( $YbCl_2$. $6H_2O$) with PyAA-$H_2$ to give the 2:1 complex [$Yb_2$ (PAA) $Cl_4$ $(H_2O)_4$. $2H_2O$ which were characterized by spectral data, electrical conductance, magnetic susceptibility, thermal and elemental analysis.

Syamal(47) synthesized a new $Cu^{2+}$- complexes of Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde and 3-aminothiophenol. The Schiff bases coordinated through O, N and S as tridentate dibasic ligands. The complexes, which are characterized by elemental analysis, ir and electronic spectra and magnetic susceptibility measurements were insoluble in common solvents and decompose above 250°C without melting. The complexes posses subnormal magnetic moments ($\mu_{eff}$ = 1.31 - 1.54 B. M. at room temperature) and were involved in antiferromagnetic exchange with an S = O ground state. The electronic absorption spectra of the complexes exhibit one ligand field band at 15000 $cm^{-1}$.

A simple, sensitive and selective spectrophotometric method for the determination of trivalent $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Gd^{3+}$, $Dy^{3+}$ and $Eu^{3+}$ ions with 8-hydroxyquinoline-5-sulfonic acid was described(48). The optimum condition for determination of down to 10.00 μg/ml of lanthanide ions were reported. The proposed method showed an average recovery of 99.9 % with standard deviation not exceeding 0.1 %. The metal-ligand ratio and stability constants of the chelates were determined.

The composition, and protonation constants of 2N-salicylidene-5-phenyl-1,3,4-thiadiazole (SPT) and 2N-3,5-dichlorosalicylidene-5-phenyl-1,3,4-thiadiazole (DCSPT) and formation constants of their metal-chelates with $Cu^{2+}$ and $Ni^{2+}$ in 50 % ethanol - water system had been determined by Irving-Rossotti method at various ionic strength at 25 ± 1°C(49). The observed order of the ligands on the basis of relative strength was SPT>DCSPT. The order of stability of the metal chelates was found to be $Cu^{2+} > Ni^{2+}$. Solid complexes were also separated. Chemical analysis suggested a 1:2 stoichiometry of metal : ligand.

Potentiometric studies had been carried out on metal complexes of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$ with N-(2-hydroxy-1-naphthalidene)-4-carbomethoxy aniline(50). The formation constant (log K) of the reagent and the stability constants of its metal complexes had been determined by Bjerrum's method at 30 ± 0.1°C and at ionic strength 0.1 M. The order of stability constants of the chelates is found to be $Cu^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$.

Proton-ligand and metal-ligand stability constants of the Schiff base ligands N(2-hydroxy-3-methoxybenzylidene)-2-aminobiphenyl (AH) and N (2-hydroxy -3- methoxybenzylidene) -1-naphthylamine (BH) complexes with $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Mg^{2+}$ were

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determined(51) potentiometrically in 75 % (v/v) dioxan-water medium having a constant ionic strength 0.1 M at 30 ± 0.1°C. The stability constants of complexes of bivalent metal ions with the ligands AH and BH were in good agreement with **Irving - Williams** methods.

**Sengupta et.al**(52); studied the complexation equilibria of metal complexes of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Zn^{2+}$ with Schiff base ligand salicylidene sulphanilamide (SASUD). The proton dissociation constant of the reagent and the stability constants of its chelates had been determined by **Bjerrum-Calvin** pH titration technique as adopted by Irving and Rossotti in 50 % (v/v) aqueous ethanol medium in different ionic strengths at 42°C ($\mu$ = 0.1, 0.05, 0.01 M $KNO_3$) and at 32°C ($\mu$ = 0.1 M $KNO_3$). The order of the stability constants of the chelates was found to be $Mn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$.

**Sengupta et.al**(53); investigated the salicylidene anthranilic acid (SAA) complexes of trivalent Pr, Nd, Sm and Gd in 50 % (v/v) ethanol-water medium at two temperatures 32 and 42 ± 1 °C and at approximately constant ionic strength ($\mu$) of 0.1 M ($NaClO_4$). It was observed that the stability constants show an increasing trend as the temperature decreases suggesting thereby that low temperature is favourable for complexation. The overall stoichiometric stability constants were found to be in the order, $Pr^{3+} > Nd^{3+} > Sm^{3+} > Gd^{3+}$.

**Sengupta et.al**(54); investigated the chelate formation of rare earth metal ions $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ and $Gd^{3+}$ with the Schiff base ligand salicylidene-2-iminopyridine in aquo-organic solvent systems having different dielectric constant values at 30 ± 1 °C potentiometrically. The order of stability of the metal complexes in 50 % (v/v) acetone-water

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systems was $Pr^{3+}$>$Nd^{3+}$>$Sm^{3+}$>$Gd^{3+}$ and in ethanol-water [50, 40, 30 % (v/v)] systems it was $Pr^{3+}$>$Nd^{3+}$< $Sm^{3+}$>$Gd^{3+}$. Such observed changes in the stability order in aquo-organic media of different dielectric constants may be due to the role played by the electrostatic and non-electrostatic parameters of the medium(55,56).

Proton-ligand and metal-ligand stability constants of the Schiff bases of 2-salicylaldiminothiazole ($SB_1$) and 2-Salicylalimino-4-phenylthiazole ($SB_2$) complexes with $La^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$ and $Ho^{3+}$ were determined potentiometrically(57) in 20 % (v/v) methanol-water at 20°C and a constant ionic strength of 0.1 M $NaClO_4$. A regular increase of stability constants was obtained form lanthanum to holmium with the exception of gadolinium due to the combined effect of ligand field stabilization and the hydration number of the metal ions. The chelate formation also contributes to the greater stability of the present complexes.

The proton-ligand stability constants of salicylaldehyde, 3-methylsalicylaldehyde, 4-methylsalicylaldehyde, 5-methylsalicylaldehyde and 5-bromosalicylaldehyde and stability constants of their complexes with $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Mg^{2+}$ have been determined(58) in ethanol-water medium (50 % v/v) at $\mu = 0.1$ ($NaClO_4$) and 25°C. The order of stability constants was found to be Cu>Co>Ni>Mn>Zn>Cd>Mg, which is in agreement with the Irving-Williams order of stability of bivalent metal complexes.