CHAPTER ONE

INTRODUCTION

The complexes, in which the metal ion has two or more types of ligands in its coordination sphere, are termed mixed ligand complexes. The ligands may be unidentate or polydentate. In the latter case the complex is known as heterochelate.

The mixed complexes of the type $[Co(NH_3)_xCl_4]$ were known since the time of Werner, and there exists enormous possibilities of their formation in the solution. Even an apparently binary complex may have solvent molecule coordinated to the metal and may be a ternary complex. The mixed ligand complexes hava a predominant role to play as reaction intermediates in catalysis and also in enzymatic reactions in biochemical systems.

In the systems containing one metal and two ligands, with significant difference in complexing tendencies, simple complex is formed between the more complexing ligand and the metal ion, whereas, the other ligand remains unbound in solution. However, if the complexing tendencies do not differ very much, following types of reactions take place, leading to the formation of mixed ligand complexes[1].

(1) Coordination of the metal ion with both ligands simultaneously to form a mixed ligand chelate in a single step or two overlapping steps, reflecting slight difference in the affinities of the ligands for the metal ion.

$$M + A + L \rightleftharpoons MLA$$

$$M + L + A \rightleftharpoons MA + L \rightleftharpoons MAL$$

(II) Formation of a mixed ligand chelate in two distinctly separated steps, reflecting a large difference in the affinities of the ligand for the metal ion.

$$M + A \rightleftharpoons MA$$

$$MA + L \rightleftharpoons MAL$$

In the reaction of the first type the solution consists of the species MA, ML, MAL, MA_2 and ML_2, formation of each being governed by a formation constant. The following reactions can lead to the formation of the mixed ligand complex MAL and four different formation constants have to be considered.

$$MA + L \rightleftharpoons MAL \qquad K_1 = [MAL] / [MA]\,[L]$$

$$ML + A \rightleftharpoons MAL \qquad K_2 = [MAL] / [ML]\,[A]$$

$$M + A + L \rightleftharpoons MAL \qquad K_3 = [MAL] / [M]\,[A]\,[L]$$

$$MA_2 + ML_2 \rightleftharpoons 2MAL \qquad K_4 = [MAL]^2 / [MA_2]\,[ML_2]$$

The study of such systems has been carried out by Watters and coworkers.[2-4] They have worked out on systems MAL where M = Cu(II), Ni(II), Zn(II) and Cd(II); A = ethylenediamine and L = oxalic acid, using potentiometric and spectrophotometric techniques. The equilibrium constants of the formation of Hg(II) salts containing one halide and another pseudohalide have been determined[5] and the method has been extended to the case of mixed ligand complex, Hg(II) cyanide-halide by Beck and Gaizer.[6] Newman and coworkers[7] have used spectrophotometric method for the mixed halide complexes of Bi(III). Nasanen and coworkers[8,9] and Perrin and Sharma[10-12] have also extensively worked out such ternary complexes. Mixed ligand complexes containing two optical isomers of the same ligand coordinating to the metal ion have also been studied.[13]

In the second type of reaction the species present in the solution can be MA and MAL. There is only one mixed ligand formation constant which characterises the reaction $MA + L \rightleftharpoons MAL$

$$K^{MA}_{MAL} = [MAL]/[MA][L]$$

The necessary condition for such a system is that the two ligands must combine with the metal ion in the different pH ranges. The formation of $[MA]$ complex tshould take place at a lower pH and it should be stable upto higher pH.[14] In 1:1 complex $[MA]$, the remaining coordination positions of the metal ion are occupied by water molecules. On the addition of a secondary ligand L, water molecules are displaced resulting in the formation of the mixed ligand complex $[MAL.]$

Several systems of the above types have been studied. Punger and coworkers[15] employed the high frequency titrimetry to study the complexes of Ni(II) with dimethylglyoxime and dipyridyl. Potentiometric and spectrophotometric titrations of dicyano-bis(dipy) iron(II) and dicyano-bis(1,10-phen) iron(II) in acetic acidwere carried out.[16] The formation constants of Fe(II) complexes of dipyridyl and its 4,4'-disubstituted derivatives in glacial acetic acid were determined by spectrophotometric method.[17] Schillt[18] used the complex, dicyano-bis(1,10-phen)Fe(II). 2.H_2O (Ferrocy.phen) and dicyano-bis(2,2'-dipy)Fe(II).3H_2O (Ferrocy. dipy), as indicator in redox determination of aqueous solution of p-$C_6H_4(OH)_2$ and primary aromatic amines. Atkinson and coworkers[19] studied the chelate effect by carrying colorimetric, potentiometric and electron spin resonance spectral studies of mixed ligand complexes of dipy and pyridine with many first row transitional metals. The mixed ligand complexes $[Co(III)(dipy)Y.Cl_2]X$ where Y is a bidentate amino acid were examined polarographically.[20] The solution stabilities of mixed ligand complexes of the type $[Cu(dipy)(L)]$ where L is polyhydroxyphenols and acids have been reported by Martell and coworkers.[21] Potentiometric titration technique has been used in the study of binuclear diolated Cu(II) complexes of $[Cu_2(OH)_2L_2]^{2+}$ ion, where L = dipy. or o-phen or histamine.[12] Sigel and coworkers[22-25] have investigated ternary transition metal complexes with dipyridyl as the primary ligand and many monodentate or bidentate secondary ligands coordinating through two oxygen atoms, two nitrogen atoms or one oxygen and one nitrogen atom. Lal and Agarwal[26] determined the formation constants and synthesised the heterochelates containing oxo.vanadium(IV) o-phenanthroline and eighteen dihydric phenolic compounds. The ternary complex in solution, where dipyridyl is used as the primary ligand and aliphatic and aromatic acids are the secondary ligands, have been reported.[27] An emf method was used to study the interaction of tris(2,2'-dipyridyl)Co(III) with halide, carbonate, sulphate and selenite ions at 25°C and stability constants of the complexes formed were determined.[28] Sigel and coworkers[29] reported the stability constant of 2,2'-dipyridyl.Cu(II)pyrocatechol complex. The ternary transition metal complexes with dipyridyl have been reported by Griesser and Sigel.[30] They[31] have also determined the rate constant for the formation and dissociation of the mixed ligand complex $[Cu(dipy)(gly)]^{2+}$ using temperature jump technique. The stability constants of mixed complexes of Cu(II) with 2,2'-dipyridyl and picolinic or 6-methyl picolinic acids were determined.[32] Stability of silver and cadmium complexes with 2,2'-dipyridyl in aqueous-organic solutions were determined.[33] The mixed ligand complex studies in solution, where dipyridyl or o-phenanthroline is the primary ligand and the amino acids polyhydroxy phenols, thioacids, are the secondary ligands have been reported from our laboratory.[34-41]

The systems Cu(II) bis(carboxymethyl)dithiocarbamate-o-phen (or dipy) were studied spectrophotometrically and the stability constants were determined graphically.[42]

The experimental methods for the determination of the mixed ligand complex formation constants have been discussed by Beck.[43] Sigel used pH metric method for the calculation of formation constants in the reaction of the second type.[30] He calculated K^{MA}_{MAL} considering the reaction to be strictly of the type $MA + L \rightleftharpoons MAL$ and also by considering it to be of the first type i.e. involving species ML and the step $ML + A \rightleftharpoons MAL$. The values worked out to be almost same. We have suggested an extension of Irving-Rossotti titration technique for the study of such systems.[34,44]

It has been observed by Watters and coworkers[2,3] that in the mixed ligand system MAL where A = ethylenediamine and L = oxalate ion, K^{MA}_{MAL} is lower than K^{M}_{ML}. This is a statistical requirement. The ethylenediamine molecule has a greater σ-bonding tendency than water molecule, and thus increases the concentration of electrons around the metal ion and hence the tendency of the oxalate ion to get bound with $[M(en)]^{2+}$ is less than the tendency to get bound with aquated metal ion.

It has been observed that mixed ligand formation constant K^{MA}_{MAL} is significantly larger than would be expected from statistical considerations. K^{MA}_{MAL} has much higher value than $K^{ML}_{ML_2}$. This has been explained[34-41] in terms of charge. The ternary system [Cu.en.oxalate] is neutral whereas bis oxalate Cu(II) complex ion has two negative charges. There is no coulombic repulsion between neutral ethylenediamine molecule and the oxalate ion during the formation of $[\mathrm{M.en.oxalate}]$ and hence the enthalpy change is more. Since the molecule is neutral,there is no solvation and the entropy change is positive. Thus both the entropy and enthalpy factors favour the formation of $[\mathrm{M.en.oxalate}]$ and hence K^{MA}_{MAL} has higher value than $K^{ML}_{ML_2}$.

Dipyridyl and o-phenanthroline are neutral molecules and should behave like ethylenediamine. It is, however, interesting to note that the formation constant K^{MA}_{MAL}, where A = dipyridyl or o-phenanthroline is only slightly lower than $K^{M}_{ML_1}$ and is much higher than $K^{ML}_{ML_2}$. This can be attributed to the special behaviour of dipyridyl and o-phenanthroline molecules.[27,29,45,46] They are bound to the metal ion by σ-bond as in case of ethylenediamine. Beside, that, there is also π-bond formation by the back donation of electrons from the metal $d\pi$-orbitals to the delocalised π-orbitals over the ligand. The $d\pi$-$p\pi$ interaction does not allow the concentration of electrons on the metal ion to increase significantly. In other words, the positive charge on the metal ion in $[\mathrm{M.dipy}]^{2+}$ is almost same as in $[\mathrm{M(aq)}]^{2+}$ complexes. The enthalpy change in the coordination of L^{2-} with $[\mathrm{M(aq)}]^{2+}$ or $[\mathrm{M(dipy)}]^{2+}$ can be expected to be same. Since the species $[\mathrm{ML}]$ and $[\mathrm{MAL}]$ are both neutral, the entropy change will also be same in both the cases. This explains why $K^{MA}_{MAL} \approx K^{M}_{ML}$. It has been observed by Sigel and coworkers[22-25] and also by Bhattacharya and coworkers[34-41] that $K^{M}_{ML} - K^{MA}_{MAL}$ is least when L is a ligand with two oxygen as coordinating atoms. The difference increases when coordination is from one oxygen and one nitrogen.

Sigel[30] has put forth two explanations. The π system of the oxygen containing ligand may have some effect. There may be an interaction between the metal $d\pi$ orbital, π orbital over dipyridyl molecule and delocalised π electron cloud over the catecholate ion. Ligands with oxygen and nitrogen as coordinating atoms or two nitrogen atoms do not have delocalised π electron clouds. This is, however, not very convincing because the metal having donated π electron to dipyridyl molecule should have less tendency to undergo π interaction with catecholate ion. This effect, if possible, should decrease rather than increase the value of K^{MA}_{MAL}. Another explanation is in terms of Pearson's "hard and soft rule".[47] As a result of back donation of electrons from the metal d orbitals to dipyridyl, the metal ion becomes a harder acid. This favours coordination with oxygen than with nitrogen ligand.

In the present investigation systems M.dipy.L, where L = diamines with two coordinating nitrogen atoms, have been studied.

Mixed ligand complexes containing charged ligand ions as primary ligand have also been studied earlier.[48-51] Mixed coordination of metallic ions with compounds of biological interest, for example the system containing Zn(II).histidine.CN$^-$, was studied potentiometrically by Martin and coworkers.[52] They also studied the system Cu.histidine.threonine both potentiometrically and by X-ray crystallographic analysis.[53] Various mixed ligand complexes with iminodiacetic acid as the primary ligand have been studied.[54,55] The mixed ligand complexes of the type Ni.IMDA.L where L = pyridine, ammonia or water have been studied by Fridman and coworkers.[56] Potentiometric studies on stepwise mixed ligand complex formation involving IMDA as the primary ligand were carried out by Sharma and Tondon.[57,58] They have also reported[59] the mixed ligand formation constants of the ternary system [M.IMDA.L] where M = Cu(II), Ni(II), Zn(II) or Cd(II) and L = glycine, α-alanine, dl-aspartic acid, 1,2-propylenediamine, salicylic acid, sulphosalicylic acid, chromotropic acid or tiron. The formation constants of the complexes of the type [Cu.AL] where A = IMDA, and L = pyridine or n-butylamine were studied by potentiometric method.[60] Israeli[61] studied the formation constants of mixed ligand complexes of Cu(II) and Ni(II) with NTA, and glycine and other mixed ligand systems. Kirson and coworkers[62] reported the triple complexes [Cu.en.NTA] and determined its instability constant. A pH metric method has been employed to measure the solution stabilities of the ternary systems of Be(II) containing NTA and Tiron.[63] Daytlova and coworkers[64] studied the behaviour of aqueous solution of Be(II) in the presence of amino polycarboxylic acid. Martell and coworkers[1] have determined the stability of the ternary complexes containing U(VI) NTA and hydroxyquinoline sulphonic acid, using their own method based on the consideration that U(VI) NTA complex formed at lower pH combines with the secondary ligand at higher pH. Vehava and coworkers[65] reported the Cr(III) complexes with NTA as a tridentate or tetradentate ligand. Solution equilibrium between Eriochrome Black T and Zn(II) NTA has been studied spectrophotometrically.[66] Equilibrium and stereochemical studies of the interactions of amino acids and their esters with bivalent metal nitrilotriacetic acid complex have been carried out.[67] A pH metric study of the ternary systems

M.NTA.glycine where M = Cu(II), Ni(II), Zn(II) has been reported.[14] Israeli and coworkers[68-71] studied the mixed ligand complexes of Cu(II) and Ni(II) with NTA and amino acid by using spectrophotometric method. Potentiometric studies of stepwise formation of complexes containing Cu(II), Ni(II), NTA and hydroxy acid were also reported by Tondon and coworkers.[72] The system (M.NTA.L) where L = picoline, oxime, serine, arginine and ammonia have also been studied.[73,74] The potentiometric titrations of Cu(II) with NTA, with a copper wire as indicator electrode were carried out.[75] Freeberg[76] employed thermometric titrations to study nitrilotriacetate complexation reaction with bivalent metal ions. Complexes of the type M.NTA.L where M = Cu(II), Ni(II), Zn(II), Cd(II) and L = amino acids, polyhydroxy phenol and mercapto acids have been reported from our laboratory.[77-81] Other systems, where dyes[82] and Schiffbases[83] are primary ligands and amino acids or hydroxy acids are the secondary ligand have also been studied.

In all the above 1:1 complexes of the multidentate amino polycarboxylate ions the remaining coordination positions of the metal ions are occupied by water molecules. On the addition of a secondary ligand the water molecules are displaced resulting in the formation of the mixed ligand complex $[MAL]^{n-}$. The method for the determination of the formation constants in such systems have been discussed in the monograph by Beck.[43] An extension of Irving-Rossotti titration technique has also been used for the study of such complexes.[77-81]

In the cases of above complexes, where primary ligand is a charged ion, K^{MA}_{MAL} values are significantly lower than the values of K^{M}_{ML}. This can be explained to be due to repulsion between the already existing charged ion Hist.(-1), IMDA (-2), NTA (-3), EDTA (-4) and the secondary ligand L^{n-}. Thus the tendency of the secondary ligand to combine with MA will be less than to combine with $[M(H_2O)_n]^{2+}$ and this results in the lowering of the values of K^{MA}_{MAL}. If the repulsion between A^{n-} and L^{n-} is more than between L^{n-} and the incoming L^{n-}, K^{MA}_{MAL} may be even less than $K^{ML}_{ML_2}$. The difference $K^{M}_{ML_1} - K^{MA}_{MAL}$ is more with the increasing charge of L^{n-}. The mixed ligand formation constants are also dependant on the nature of A^{n-}. For the complexes $[MAL]^{X-}$ with different A^{n-}, the following order holds good;

$$K^{M.Hist.}_{M.Hist.L} > K^{M.IMDA}_{M.IMDA.L} > K^{M.NTA}_{M.NTA.L} > K^{M.EDTA}_{M.EDTA.L}$$

This can be explained by considering that the electrostatic repulsion between the primary ligand and secondary ligand goes on increasing with the increase in the charge on the primary ligand. The values of the formation constants of the complexes [M.HIST.L] and [M.IMDA.L] are very close though Histidine has one negative charge and IMDA has two negative charges. This may be because histidine is a bigger molecule and causes more steric hindrance to the incoming secondary ligand ion. Steric factor is also operative in EDTA complexes. It is observed that the difference $K^{Cd}_{Cd.L} - K^{Cd.EDTA}_{Cd.EDTA.L}$ is less than $K^{Zn}_{Zn.L} - K^{Zn.EDTA}_{Zn.EDTA.L}$.84 This is because cadmium ion with bigger size has greater space and hence steric hindrance due to EDTA is less. It is also worthwhile to study the ternary complexes where A is a charged ion as above and L is a neutral diamine. Such studies have been carried out in the present investigation.

The systems studied in the present thesis are ML and MAL where M = Cu(II), Ni(II), A = dipyridyl, o-phenanthroline, histidine, IMDA and NTA and L = ethylenediamine, propylenediamine, 1,3-diaminopropane, N-methyl en, N-ethyl en, N-N'-dimethyl en, N-N-dimethyl en and N-N-diethyl en. The compounds with ethylenediamine and propylenediamine have been isolated, and characterised.

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