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Stability constants of mixed ligand complexes of Cu(II) ion with 5-Methyl- OHA-N-(4'-methyl phenyl) imine (R_1) and amino acids & 5-Methyl- OHA-N-(4'-methoxy phenyl) imine (R_1) and amino acids in 50 % (v/v) ethanol - water mixture.

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ABSTRACT

For the measurements of stability constants of metal complexes, PH-metry is one of the most convenient and successful technique can be employed. In the present work, we investigated the stability constants of mixed ligand complexes of transition metal ion Cu (II) with 5- methyl – OHA- N- (4'- methyl phenyl) imine, 5-methyl-OHA- N-(4'- methoxy phenyl) imine and a series of seven amino acids in 50% (v/v) ethanol- water medium having 0.1 M (NaclO4) ionic strength. The present work was under taken to study the mode of formation of mixed ligand chelates of Cu (II) with Schiff's bases & amino acids.

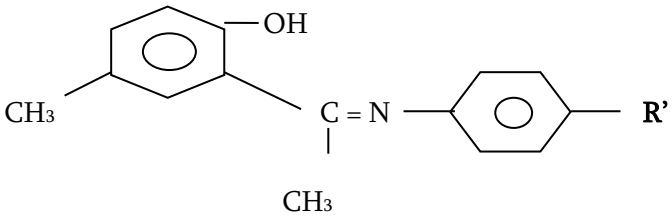
Keywords :- PH- metry, stability constant, mixed ligand complex, transition metal, Schiff's base, amino acids.

I. INTRODUCTION

The study of mixed ligand complexes continues to attract many researchers because of their novel structural features, interesting spectral and magnetic properties and applications in various industries. The condition required for the complex formation may be predicted on the basis of its stability constants in solutions. The considerable research activity has been centered on mixed ligand complexes in recent years.[1-7] Mixed ligand complexes are quite common in biological and analytical systems.[8-9] Mixed chelation commonly occurs in biological fluids as millions of potential ligands are likely to compete for metal ions found in vivo i.e. Na, K, Mg, Ca, Mn, Fe, Co, Cu, Zn, Mo. Etc. Mixed coordination by proteins and related substances has been a subject of investigation of many workers.[10-16] The formation of mixed ligand Complexes is also important in understanding the behavior of pollutants in natural water.[17] The molecular formula & structures of Schiff bases R_1 & R_2 used for present study are given below.

R_1: 5-Methyl- OHA-N-(4'-methyl phenyl) imine, M.F.:- $C_{16}H_{17}ON$

R_2: 5-Methyl- OHA-N-(4'-methoxy phenyl) imine, M.F.:- $C_{16}H_{17}O_2N$



In $R_1 \rightarrow$ **R'** = CH_3
In $R_2 \rightarrow$ **R'** = OCH_3

II. Experimental Details

All the chemicals used were AR grade. All the solutions were prepared in double glass distilled water. The purity of Schiff bases was checked by nitrogen analysis and IR- spectra. The amino acids were recrystallized and their purity was checked by their melting points. Schiff bases R_1 and R_2 were used as primary ligands (R) and a series of seven amino acids like Glycine, Leucine, Methionine, Tryptophan, DL-Valine, DL-Alanine, and DL-phenyl alanine were used as secondary ligands (B). The present study was undertaken to explain the variation in the stability constants in terms of Δlog K, K_R, K_B, and K_r values. Each Schiff base (R_1 & R_2) was used as primary ligand with seven amino acids. The total number of mixed ligand systems studied were fourteen which are as follows.

1. 5-Methyl- OHA-N-(4'-methyl phenyl) imine - Glycine
2. 5-Methyl- OHA-N-(4'-methyl phenyl) imine -Leucine
3. 5-Methyl- OHA-N-(4'-methyl phenyl) imine -Methionine
4. 5-Methyl- OHA-N-(4'-methyl phenyl) imine -Tryptophan
5. 5-Methyl- OHA-N-(4'-methyl phenyl) imine – DL-Valine
6. 5-Methyl- OHA-N-(4'-methyl phenyl) imine –DL-alanine
7. 5-Methyl- OHA-N-(4'-methyl phenyl) imine - DL-Phenyl alanine
8. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine - Glycine
9. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine -Leucine
10. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine -Methionine
11. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine -Tryptophan
12. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine -DL- Valine
13. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine -Dl- alanine
14. 5-Methyl- OHA-N-(4'-methoxy phenyl) imine–DL-Phenyl alanine.

Simplest case of mixed ligand complex formation is to be coordination of two different ligands with the central metal ion, then the following Equilibrium and Equilibrium constants must be considered.

$$M + R \rightleftharpoons MR \qquad K_{10} = \frac{[MR]}{[M][R]}$$

$$MR + R \rightleftharpoons MR_2 \qquad K_{20} = \frac{MR2}{(MR)(R)}$$

$$K_{10}.K_{20} = B_{20}$$

$$M + B \rightleftharpoons MB \qquad K_{01} = \frac{MB}{(M)(B)}$$

$$MB + B \rightleftharpoons MB_2 \qquad K_{02} = \frac{MB2}{(MB)(B)}$$

Mixed ligand complexes: K_R

$$MRB \rightleftharpoons MR + B \qquad K_A = \frac{MRB}{(MR)(B)}$$

$$MRB \rightleftharpoons MB + R \qquad K_B = \frac{MRB}{(MB)(R)}$$

$$MRB \rightleftharpoons M + R + B \qquad \beta_{11} = \frac{MRB}{(M)(R)(B)}$$

$$2MRB \rightleftharpoons MR_2 + MB_2, \qquad K_r = \frac{[MRB]2}{(MR2)(MB2)}$$

The K_r, K_B, K_r, β_{11}, β_{20}, β_{02}, values for mixed ligand complexes of Schiff bases (R_1 and R_2) with amino acids are calculated and set out in table 1.1, to 1.2 , All the values are in log units.

Table: 1.1- Stability constants and some Parameters based on some relationships between formation of mixed ligand complexes of Cu (II) with 5-Methyl- OHA-N-(4'-methyl phenyl) imine (R_1) and amino acids.

Amino acids	β_{11}	β_{20}	β_{02}	K_B	K_R	Kr	Δ log K
Glycine	16.69	15.80	14.71	8.87	7.82	1.09	0.00
Leucine	14.00	16.31	14.71	6.18	5.10	9.90	-2.72
Mithionine	15.99	15.92	14.71	8.17	7.42	1.04	-0.40
Tryptophan	15.87	16.62	14.71	8.05	6.89	1.01	-0.93
DL- Valine	16.29	16.91	14.71	8.47	7.01	1.03	-0.81
DL- Alanine	14.38	16.86	14.71	6.56	5.15	0.91	-2.67
DL- Phenyl alanine	16.58	15.79	14.71	8.76	7.82	1.08	0.00

Table: 1.2- Stability constants and some Parameters based on relationships between formation of mixed ligand complexes of Cu (II) with 5-Methyl- OHA-N-(4'-methoxy phenyl) imine (R_2) and amino acids.

Amino acids	β_{11}	β_{20}	β_{02}	K_B	K_R	Kr	Δ log K
Glycine	16.38	15.80	14.91	8.37	7.51	1.06	-0.50
Leucine	16.90	16.31	14.91	8.89	8.00	1.08	-0.01
Mithionine	16.50	15.92	14.91	8.49	7.93	1.07	-0.08
Tryptophan	16.97	16.62	14.91	8.96	7.99	1.06	-0.02
DL- Valine	16.04	16.91	14.91	8.03	6.76	1.00	-1.25

DL- Alanine	17.24	16.86	14.91	9.23	8.01	1.08	-0.05
DL- Phenyl alanine	14.99	15.79	14.91	6.98	6.23	0.78	-1.78

III. RESULTS AND DISCUSSIONS

The negative Δ log K for ternary system indicates that the primary ligand anion and secondary ligand anion preferentially form ternary complexes to the binary ones. The values of β_{20}, β_{02}, K_B, K_R, and K_r were calculated for all the systems and presented in the same table. There values were calculated to discuss the effect of displacement of one ligand by the other on the strength of metal ligand bond. The perusal of the values of log from table 1.1 and 1.2 shows that the order of stability of ternary complexes of Cu (II) – R_1 - system with respect to secondary ligands is $B_1 > B_7 > B_3 > B_5 > B_4 > B_6 > B_2$ and of Cu (II) – R_2 - system with respect to secondary ligands is $B_2 > B_4 > B_6 > B_3 > B_1 > B_5 > B_7$

It can be seen from Table 1.1 and 1.2 that the K_r values are positive for all the ternary chelates investigated in the present work which shows that $\beta_{11} > \beta_{20}. \beta_{02}$. In addition to K_r, two more constants K_R and K_B are calculated and used to discuss the relative stability of mixed ligand and binary complexes. In Cu (II) chelates of R_1 - amino acids, K_B is greater than K_{20} for all the systems except DL- alanine and leucine. The same trend is seen in R_2- amino acids system. Similarly, $K_{B8} > K_{02}$ for all the systems except where amino acids are DL- alanine and leucine. The positive values of Kr and the trend exhibited by K_R and K_B reveals that the ternary chelates of all the systems are more stable than their corresponding binary systems.

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