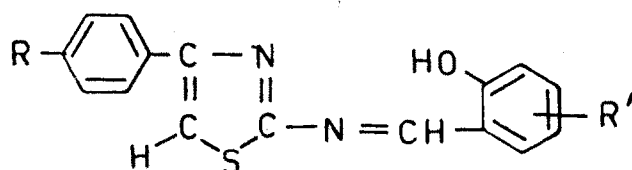


CHAPTER - IV

CHAPTER - IVGENERAL DISCUSSION :

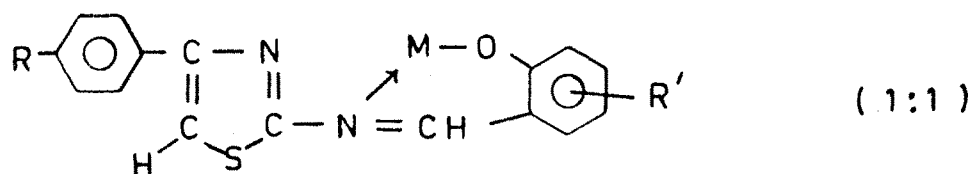
The complex formation with schiff bases takes place because of the presence of lone pair of electron on the nitrogen atom and by virtue of the general electron donating character of the double bond thereby attributing basic properties to the compounds containing the azomethine group. The general structure for the selected Schiff bases is given below :

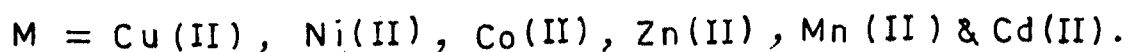
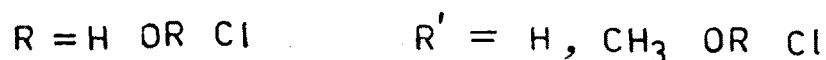
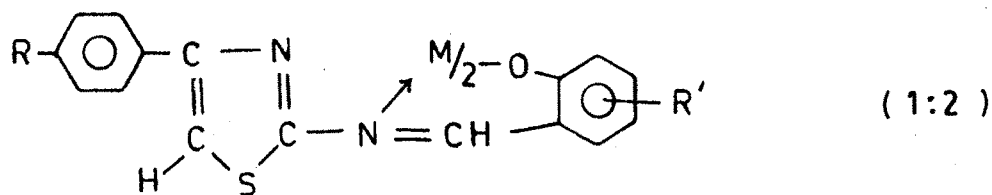


R = H OR Cl

R' = H, CH₃ OR Cl

Schiff bases and its substituted analogous have phenolic OH group available for abstraction of the proton. The metal ion forms M-O bond. Nitrogen atom of azomethine group donates a pair of electron to form coordinate bond with metal ion. In solution 1:1 and 1:2 complexes are defected.



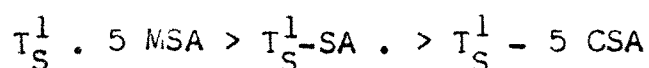


From titration curves, the average number of ligands attached per metal ion (\bar{n}) and free ligand exponent (pHL) were calculated using the method of Irving and Rossotti (1) from the values of n and pHL, the formation curves were plotted and the formation constants were determined by half integral and graphical methods (2-4).

Proton ligand stability constants :

In the ligands it is phenolic -OH group which take part in the complex formation and hence the number of dissociable protons present in the ligand molecules is one. The ligand titration curves shifted above the acid titration curve due to the basic property of the ligand that azomethine nitrogen accepts proton from strongly acidic medium. In the basic region the curve lies below the acid curve due to the release of -OH protons.

The pK values of $T_S^1\text{SA}$, $T_S^1.5\text{MSA}$ and $T_S^1-5\text{-CSA}$ are in the following order.



and pK values of $T_S^4\text{-SA}$, $T_S^4.5\text{MSA}$ and $T_S^4-5\text{CSA}$ are in the order

$$T_S^4 - 5 \text{ MSA} > T_S^4 \text{ SA} > T_S^4 - 5 \text{ CSA.}$$

It has been observed that the pK values exhibit correlation between nature of substituent groups and stability constants. In our study we have found that as the electron withdrawing nature of substituent on the phenyl ring (of 4-aryl amino moiety) increases, the magnitude of the pK values decreases. The three substituent groups were H, CH₃ and Cl in substituted aldehyde.

The pK_{OH}^H values of the schiff bases are higher than that of corresponding Vic hydroxy aldehydes is probably due to stronger hydrogen bonding with the more basic nitrogen atom. (5). Hovey et al (6) in discussing the hydrolytic tendencies of schiff bases have attributed the higher stability of the aromatic derivatives to an increase of resonance energy in the system brought about by presence of aromatic groups.

The plot of Hammett ρ values for the chlorine and methyl substituent in five position to OH group against pK values gives straight line as shown in fig. 3.27 to 3.28

ρ - values for substituent groups

<u>Group</u>	<u>ρ</u>
H	0
5Cl	+0.23
5CH ₃	-0.17

The values of ρ constants are taken from Barton and Perrin (7) By applying the consideration of Biggs and Robinson (8) and further extending it to multiple functional group molecules (9-10), we get equation

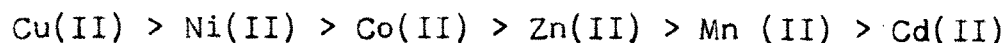
$$\left. \begin{aligned} \text{pK}_1^{\text{H}} &= 11.65 - \rho \sum \sigma \\ &= 11.65 - 3.5 \sum \sigma \end{aligned} \right\} \text{T}_S^1\text{-SA}$$

$$\left. \begin{aligned} \text{pK}_1^{\text{H}} &= 11.45 - \rho \sum \sigma \\ &= 11.45 - 3.5 \sum \sigma \end{aligned} \right\} \text{T}_S^4\text{-SA}$$

Metal Ligand Stability Constants :

The occurrence of the metal titration curves below the ligand titration curve at pH values much below the pH of metal ion hydrolysis confirmed the complexation between the ligand and metal ion. The proton of the phenolic - OH group was replaced by the metal ion and chelation took place through Phenolate oxygen and azomethine nitrogen. The metal ligand formation curves suggested 1:1 and 1:2 complexes.

The results of this study indicated that in general the formation constants of chelates increase with an increase in the basicity of the nitrogen atom. The stability constants order in the present work was



The order of stabilities agrees well with that reported by Irving Williams, Mellor and Maley (11-13).

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