Summary and Conclusion

Thiazoles are well known as biologically active compounds. Literature survey reveals that Schiff bases containing thiazole ring exhibit pronounced antibacterial and antifungal activities. A lot of work has been done to study structural aspects and evaluation of biological activities of transition metal and rare earth complexes of Schiff bases because these ligands possess strong synthetic flexibility and selectivity towards metal ions.

Schiff bases exhibit interesting reactions namely addition, cycloaddition, reduction and photochemical reactions. Elemental and spectral (uv – visible, IR, ESR and mass) analyses, magnetic and thermal studies, and XRD analysis of metal complexes of Schiff bases have made good contribution to the field of coordination chemistry. Potentiometric and pH metric studies on formation of metal complexes with Schiff bases in mixed solvent (for example: ethanol – water, methanol – water and dioxan – water etc) have created huge interest among researchers.

In this thesis entitled “studies on transition metal complexes with thiazole ring containing ligands”, we have reported determination of proton ligand stability constants of Schiff bases derived from substituted 2-aminothiazoles and O-hydroxyaldehydes (series I and II) as represented below

Series I : Schiff bases (LH) derived from 4-(p-bromophenyl)-2-
aminothiazole

1) SBPAT : N-(salicylidene)-4-(p-bromophenyl)-2-aminothiazole.

2) HNBPAT : N-(2-hydroxy-1-naphthalidene)-4-(p-bromophenyl)-2-
aminothiazole.

3) 5MSBPAT : N-(5-methylsalicylidene)-4-(p-bromophenyl)-2-
aminothiazole.

4) 4MSBPAT : N-(4-methysalicylidene)-4-(p-bromophenyl)-2-aminothiazole.

5) 5MSBPAT : N-(5-bromosalicylidene)-4-(p-bromophenyl)-2-aminothiazole.

Series II : Schiff bases (LH₂) derived from 2:4 diamino-5-chlorothiazole.

1) (HN)₂DCT : N-bis(2-hydroxy-1-naphthalidene)-2:4-diamino-5-chlorothiazole.

2) (5CS)₂DCT : N-bis(5-chlorosalicylidene)-2:4diamino-5-chlorothiazole.

3) (5MS)₂DCT : N-bis(5-methylsalicylidene)-2:4diamino-5-chlorothiazole.

4) (4MS)₂DCT : N-bis(4-methylsalicylidene)-2:4diamino-5-chlorothiazole.

And metal-ligand stability constants of their metal (Co¹¹, Ni¹¹, Cu¹¹ and Zn¹¹) complexes. The thesis consists of six chapters.

Chapter I : This chapter deals with literature survey on

- Structural studies on metal complexes of aminothiazole and thiazole ring containing Schiff bases.
- Evaluation of biological activities of thiazole Schiff bases and their metal complexes.
- Determination of proton-ligand stability constants of Schiff bases and metal-ligand stability constants of their metal complexes.
Chapter II: In this chapter we have summarized various methods used for determination of stability constants namely

- Graphical method
- Bjerrum method
- Interpolation half integral values
- Schwarzenbach’s graphical method
- Rossotti and Rossotti graphical method
- Least square method
- Bjerrum mid-point method
- Computer method

Chapter III: This chapter deals with

- Purification of solvents
- Synthesis of Schiff bases and their characterization by elemental and spectral analysis
- Experimental methods used for the determination of proton-ligand and metal-ligand stability constants
- Testing of biological activities of the ligands by using cup plate method.

Chapter IV: In this chapter we have included pH metric studies of Schiff bases of

- Series I – (SBPAT, HNBAPT, 5MSBPAT, 4MSBPAT, and 5BSBPAT)
- Series II – ((HN)$_2$DCT, (5CS)$_2$DCT, (5MS)$_2$DCT, and (4MS)$_2$DCT)

At room temperature (25$^0$C) in ethanol-water medium. The proton-ligand stability constants of the ligands have been calculated by using Half Integral and Graphical method.
We have studied the effect of substituent present in the phenyl ring to which phenolic OH and >C=N- groups are attached on the basicity of phenolic oxygen and azomethine nitrogen. We found that the +I effect (inductive effect) of methyl group as well as stronger +M effect (mesomeric effect) stronger than -I effect of halogen group increases the electron density over phenyl ring and therefore basicity of phenolic oxygen and azomethine nitrogen increases on the basis of effect of substituent present in the phenyl ring we proposed that proton-ligand stability constant values follow the order

Series I : 5MSBPAT > 4MSBPAT > 5BSBPAT > SBPAT > HNBPAT
Series II : (5MS)_2DCT > (4MS)_2DCT > (5CS)_2DCT > (HN)_2DCT

To study the effect of elevated temperature on the determination of proton-ligand stability constants, we have chosen two representative Schiff bases 4MSBPAT (series I) and (5MS)_2DCT (series II). It was found that with increases in temperature the proton-ligand stability constants values decreases.

Schiff base of series II have been screened for the evaluation of antibacterial and antifungal activities by cup plate method. The MIC values have been reported the compounds are found to possess good antibacterial activity.

Chapter V: This chapter opens with pH metric studies of complex of Schiff bases of series I and II. The metal ligand stability constants are determined by Half Integral and Graphical methods we have proposed the order of stability of the complexes which follows the trend

- Schiff base complexes of series I : Zn > Co > Ni > Cu
- Schiff base complexes of series II : Zn > Co > Ni > Cu.

The order of stability of the complexes is in accordance with that proposed by Irving and Williams.
The effect of elevated temperature on the determination of metal-ligand stability constants has been studied. It was observed that as the temperature increases the values of stability constants decrease. This suggests that low temperature is favourable for complex formation. The temperature parameter ($\Delta H$, $\Delta G$ and $\Delta S$) have been calculated. The $\Delta H$ and $\Delta G$ values are negative, whereas $\Delta S$ values are positive. The negative values of $\Delta H$ and $\Delta G$ suggest that the complex formation is thermodynamically favoured. The positive values of $\Delta S$ indicate that entropy effect is found to be predominant over enthalpy effect.