

## PREFACE

Heterocyclic Schiff base ligands play an important role in the chemistry of coordination compounds. It is due to the presence of the azomethine linkage, the Schiff bases are acting as strong chelating agents towards the transition metal ions. Many Schiff bases are used as effective corrosion inhibitors on various metals such as mild steel, copper, zinc etc. in acidic medium. The hetero atoms such as N, O, S etc. along with the imine part of the Schiff base molecules have a marked role in preventing the dissolution of metals in acidic medium. Biological applications, especially the antimicrobial power of these classes of compounds are of great importance. During the present course of investigations, seven different Schiff base ligands and their transition metal complexes were prepared and characterized. Antimicrobial studies and cyclic voltammetric studies on the metal chelates and investigations of the corrosion inhibition capacity of the newly synthesized Schiff bases have been carried out. For convenience entire work is presented in this thesis as four parts.

In the first part of the thesis seven novel potential Schiff bases such as (E)-2-(1-(pyridin-3-yl)ethylidene)hydrazinecarbothioamide(APTSC), (E)-2-(1-(pyridin-3-yl)ethylidene)hydrazinecarboxamide(APSC), (E)-3-(1-(2-phenylhydrazono)ethyl)pyridine(APPH), 4-(5-((2-carbamoylhydrazono)methyl)thiophen-2-yl)benzoic acid (CPTASC), 4-(5-((2-carbamoylhydrazono)methyl)furan-2-yl)benzoic acid (CPFASC), 4-(5-((2-phenylhydrazono) methyl)furan-2-yl)benzoic acid (CPFAPH) and 3-(furan-2-ylmethyleneamino)benzoic acid (FAABA) were synthesized and characterized. The chelating efficacy of these Schiff bases was explored by preparing metal chelates of

transition metal ions. Various physicochemical investigations have been performed on the metal chelates to elucidate their structure and geometry. Analytical tools employed are spectroscopic techniques like  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR, HMQC, COSY, DEPT 135, IR, UV-Vis spectra, magnetic moment measurements and molar conductance. Elemental analysis showed that 1:1 or 1:2 stoichiometry exist between the metal and ligand in the chelates. All the studied Schiff bases except APPH and CPFAPH were acted as monovalent bidentate ligands in metal complexes. This part is divided into five chapters. Chapter 1 consists of an introduction to coordination chemistry and a thorough review of published work on Schiff bases and metal complexes of Schiff bases derived from 3-acetylpyridine, furan-2-aldehyde and thiophene-2-aldehyde. Various physicochemical methods employed for the elucidation of the structures of the Schiff bases and their metal complexes are discussed in chapter 2. Details of synthesis and characterization of Schiff bases APTSC, APSC and APPH and their transition metal chelates of VO(II), Cr(III), Ni(II), Cu(II), Cd(II) and Ag(I) are discussed in the third chapter, as section I, II and III respectively.

Preparation and physicochemical studies on Schiff bases derived from the arylated furan-2-aldehyde and thiophene-2-aldehyde (CPFASC, CPTASC and CPFAPH) are given in the first portion of chapter 4. For the sake of discussion, this chapter is divided into three sections. First section includes the details of synthesis of transition metal complexes of CPFASC such as Cr(III), Ni(II), Cu(II) and Ag(I) and their characterization using various analytical tools. Synthesis and characterization of Cr(III), Fe(III), Ni(II), Cu(II), Zn(II) and Cd(II) chelates of the

Schiff base, CPTASC are discussed in section 2. In section 3, there is a detailed studies on the synthesis and the structural evaluation of Co(II), Cu(II) and Zn(II) metal chelates of CPFAPH. The Schiff base FAABA and its metal chelates of VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I) were synthesized and the structures were derived using various analytical techniques. The results are discussed chapter 5. This part ends with a brief summary and bibliography.

Part II deals with the detailed investigations of the corrosion inhibition capacity of the newly synthesized Schiff bases on carbon steel in hydrochloric acid medium and sulphuric acid medium. The corrosion inhibition studies were performed by conventional gravimetric studies and electrochemical analyses, such as polarization technique and electrochemical impedance spectroscopy (EIS). To predict the mechanism of corrosion inhibition by the Schiff bases, adsorption isotherms were plotted and were verified by surface morphological studies (using SEM analysis). In order to determine corrosion activation energy, entropy of corrosion, enthalpy of corrosion and Arrhenius parameters, temperature studies on corrosion were performed in the range 30-60<sup>0</sup>C. To compare the inhibition efficiencies of Schiff bases and their respective parent amines, corrosion inhibition power of the amino precursors were evaluated. An attempt was done to improve the corrosion inhibition capacity of the Schiff bases by synergistic effect with iodide ions in the corroding medium. Drastic enhancement in the inhibition efficiency was noted for certain Schiff bases in sulphuric acid upon the addition of KI. Corrosion studies clearly established that majority of the studied Schiff bases were acted as

good corrosion inhibitors on carbon steel in hydrochloric acid medium as well as in sulphuric acid medium. This part contains four chapters.

Chapter 1 report the detailed implications of corrosion related problems in various industries. Review of literature and the scope of the present study are included here. The details of different corrosion monitoring techniques are discussed in detail in chapter 2. Results and discussion of extensive corrosion inhibition research of Schiff bases, APTSC, APSC and APPH on carbon steel in 1.0 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> have been reported in chapter 3. Chapter 4 explains the corrosion inhibition investigations of the heterocyclic imines derived from furan-2-aldehyde or thiophene-2-aldehyde such as CPFASC, CPTASC, CPFAPH and FAABA on carbon steel in 1.0 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub>. The inhibitive response of 2-((5-(4-nitrophenyl)furan-2-yl)methylene)hydrazinecarboxamide Schiff base (NPFASC) are also discussed along with other four molecules. A brief summary of the corrosion studies are followed hereafter, along with the relevant references.

The details of the antibacterial investigations of newly synthesized molecules are explained in the Part III of this thesis. Plate disc and Cotton swab methods were employed for the evaluation of antibacterial and antifungal activity of the Schiff bases and their metal chelates. Microbes such as *Staphylococcus aureus*, *Bacillus subtilis*, *Bacillus thuringiensis*, *Enterobacter aerogenes*, *Escherichia coli* and *Proteus vulgaris*, were selected for the bacteriostatic analysis. Erythromycin, Streptomycin, Gentamicin, Ampicillin, Penicillin-G and Cefotaxime were taken as the standard antibiotics for comparison. DMSO was taken as the

medium for the drug dissolution. Among the studied compounds, generally metal chelates showed pronounced activity against the growth of bacteria than their parent Schiff bases. Antimicrobial investigations are presented in this part as three chapters. First chapter deals with elaborate descriptions of various microbes and the details of investigations done by earlier researchers. The scope of this study with newly synthesized molecules is also documented here. Different strategies accepted for studying the growth inhibitory power of various Schiff bases and their metal chelates on various microbes are explained absolutely in chapter 2. Results and discussion of the antimicrobial studies of various Schiff bases and their complexes are portrayed in chapter 3. This part terminates with the summary and references.

The electrochemical behavior of the Schiff bases and complexes in DMSO has been investigated by voltammetric experiments. For performing the experiment three electrode cell assembly was used in which platinum loop acted as the inert electrode, Ag-AgCl electrode performed as the reference electrode and glassy carbon electrode acted as the working electrode. Decimolar solution of tetra butyl ammonium tetra fluoro borate (TBATFB) was employed as the supporting electrolyte. Deaeration was achieved by passing nitrogen gas continuously through the medium. Out of the studied Schiff bases and complexes, only few displayed the peaks for reduction or oxidation potential and majority of the molecules behaved as quasi reversible systems. The contents in this part are subdivided into three chapters. First chapter describes general response of the organic molecule and metal ions present in chelates towards the voltammetric analysis. A detailed survey on the

literature was also reported in this chapter. The methodology accepted for performing cyclic voltammetric investigations is discussed and reported in chapter 2. Results and the discussion of various complexes and Schiff bases, which are susceptible to the redox process, are reported in chapter 3. A brief summary of these investigations are also reported at the end of this part which is followed by important references.