

PREFACE

Azomethines or Schiff base compounds and their metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. Presence of a lone pair of electrons in a sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical importance and impart excellent chelating ability especially when used in combination with one or more donor atoms close to the azomethine group. The chelating ability of the azomethine compounds combined with the ease of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting ligand in coordination chemistry. Schiff bases are present as reactants in umpteen synthetic organic processes, as important scaffolds in organometallic chemistry, as backbones of precious catalysts and as pharmaceutical presidiums against a series of different diseases and pathological states. Studies of new kinds azomethine compounds and complexes are now attracted the attention of researchers for apply in the field of corrosion and other industrial field.

In the present course of study potential azomethine class of ligands derived from polynuclear carbonyl compound and amino acids were synthesized and their structures were derived based on various analytical data. The chelating ability of these ligands with transition metal ions was also investigated. All the azomethine ligands were tested for their corrosion inhibition efficiency on carbon steel in hydrochloric acid and sulphuric acid medium. Antimicrobial activity of the Schiff bases and their metal chelates were examined using bacterial and fungal strains by paper disc diffusion method. Cyclic voltammetric studies of some synthesized compounds were also conducted. For convenience the entire work presented in this thesis is divided in to four parts.

In the first part, synthesis and characterization of six polynuclear Schiff bases, 3-(anthracen-9(10H)-ylideneamino)propanoic acid [A9Y3APA], (S)-2-(anthracen-9(10H)-ylidene amino)-5-guanidinopentanoic acid [A9Y5GPA], (S)-2-(anthracen-9(10H)-ylideneamino)-3-(1H-imidazole-4-yl)propanoic acid (A9Y3IMPA), (S)-2-(anthracen-9(10H)-ylideneamino)-3-(1H-indole-3-yl)propanoic acid (A9Y3INPA), (S)-2-(anthracen-9(10H)-ylideneamino)-3-phenyl propanoic acid [A9Y3PPA], (R)-2-(anthracen-9(10H)-ylideneamino)-3-mercaptopropanoic acid [A9Y3MPA] were described. In order to evaluate the metal binding capacity of the synthesized azomethine compounds, they were chelated with transition metal ions such as Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), and Zn(II). Various physicochemical investigations have been performed on the metal chelates to elucidate their structure and geometry. Analytical tools employed are spectroscopic techniques like ^1H NMR, ^{13}C NMR, HRMS, IR & UV-Vis spectra, magnetic moment measurements and molar conductance. Elemental analysis shown that majority of the metal chelates obeys 1:2 stoichiometry between the metal and ligand. All the studied Schiff bases acted as monovalent bidentate ligands in metal complexes, coordinating through azomethine nitrogen and carboxylate oxygen. For the detailed description of the present study, this part is divided in to eight chapters.

Chapter 1 consists of an introduction to azomethine class of compounds and a critical review of published work on Schiff bases and metal complexes. This chapter also highlights the significance and scope of the present investigation. Various physicochemical methods employed for the elucidation of the structures of the Schiff bases and their metal chelates are discussed in the chapter 2. Chapter 3 describes the synthesis and characterization of Schiff base, A9Y3APA, and its transition metal complexes with Mn(II), Fe(III), Co(II), Cu(II), and Zn(II) ions. Details of the

preparation and characterization studies of the Schiff base ligand A9Y5GPA and its transition metal chelates with Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) are reported in chapter 4. The chapter 5 contains the description about the preparation and structural evaluation of the Schiff base ligand A9Y3IMPA and its transition metal chelates with Mn(II), Fe(III), Co(II), Cu(II) and Zn(II). The Schiff base A9Y3INPA and its metal chelates of Mn(II), Fe(III), Cu(II) and Zn(II) were synthesized, the structures were derived using various analytical techniques and the results are discussed in chapter 6. The methods employed for the synthesis of a new polynuclear azomethine compound A9Y3PPA and its Cr(III), Mn(II), Fe(III), Ni(II), Cu(II) and Zn(II) complexes are well documented in the chapter 7. Synthetic and structural studies on Mn(II), Fe(III), Cu(II) and Zn(II) complexes of a newly prepared A9Y3MPA ligand are given in the chapter 8. After the chapter 8, a summary of synthesis and characterization studies of metal chelates derived from polynuclear Schiff bases are given, along with a wide spectrum of bibliography.

The part II deals with the detailed investigations of the corrosion inhibition capacity of the newly synthesized polynuclear Schiff bases on carbon steel in hydrochloric acid 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). During the polarization analysis, Tafel extrapolation method and Linear polarization method were performed separately. To predict the mechanism of corrosion inhibition by the Schiff bases, adsorption isotherms were plotted using the results obtained from gravimetric weight loss studies. Thermodynamic parameters like free energy of adsorption and adsorption equilibrium constant were also determined for confirming the nature of adsorption. 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 30-60⁰C.

To compare the inhibition efficiencies of Schiff bases and their respective parent amines, corrosion inhibition power of the amino acids were evaluated. Where the inhibition efficiency is found to be low, 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. The significant role of the halide ions in enhancing the corrosion inhibition capacity of organic molecules are verified with these studies. 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. The mechanism of corrosion was further verified with the aid of surface morphological studies. Scanning electron micrographs were very useful in predicting the nature of inhibition of the Schiff bases on carbon steel. This part contains five chapters.

The chapter 1 reports an introduction of corrosion and need for the development of new potential corrosion inhibitors. The inhibitory action of different organic molecules and amino acids on various metals in acidic medium, reported by many investigators across the world, and the scope of the present study are also included here. The details of different corrosion monitoring techniques and associated equations for determining the various corrosion parameters are discussed in detail in the chapter 2. The chapter 3 illustrates the discussion on results obtained for the corrosion inhibition studies of six amino acids on carbon steel in 1.0 M HCl and 0.5 M H₂SO₄. Results and discussion of extensive corrosion inhibition research of the newly synthesized six Schiff bases, on carbon steel in 1.0 M HCl have been reported

as well in the chapter 4. Attempts have also been made here to establish that the polynuclear Schiff base A9Y3MPA possess well accounted anticorrosion property upon carbon steel. The chapter 5 deals with the corrosion inhibition investigations of the synthesized polynuclear azomethine class of compounds, on carbon steel in 0.5 M H₂SO₄. The synergistic effect of iodide ion in the enhancement of corrosion inhibition efficiency was also studied. A brief summary of the corrosion studies are followed hereafter, along with the relevant references.

The newly synthesized Schiff bases and their transition metal chelates were subjected to antimicrobial studies. Part III explains the details of the investigations on antibacterial study. Cotton swab method and Kirby-Bauer plate disc method 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. *Aspergillus niger* is the fungal species utilized for the antifungal studies. Erythromycin, Streptomycin, Gentamicin, Ampicillin, Pencillin-G, Fluconazole and Amphotericin-B, were taken as the standard antibiotics for comparison. Diameter of microbial growth inhibition was determined in each case by triplicate measurements and averaged. Among the studied compounds, metal chelates showed distinct activity against the growth of bacteria than their parent Schiff bases. This part is segregated into 3 chapters.

The chapter 1 deals with the elaborate descriptions of various microbes and the details of investigations done by earlier researchers. The importance of the study on antimicrobial activity of these type molecules are also documented here. Different strategies accepted for studying the growth inhibitory power of the novel Schiff bases and their metal chelates on various microbes are explained absolutely in the chapter 2.

Results and discussion of the antimicrobial studies of various Schiff bases and their complexes are portrayed in the chapter 3. This part terminates with the summary and references.

The redox properties of the azomethine compounds and complexes in DMSO have been investigated by voltammetric experiments. For performing the experiment three electrode cell assemblies were 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. A scan rate of 100mV/sec was used for the analysis. Dependency of scan rate on the redox properties was also studied. The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. This data is then plotted as current (i) vs. potential (E). Out of the studied Schiff bases and complexes, only few metal chelates displayed the peaks for reduction or oxidation potential. The cyclic voltammetric studies have been divided into three chapters.

The chapter 1 describes general response of the organic molecule and metal ions present in chelates towards the voltammetric studies. The methodology accepted for performing cyclic voltammetry is discussed and reported in the chapter 2. The chapter 3 includes the results and the discussion of few complexes and azomethine compounds, which are susceptible to the redox process under the conditions of cyclic voltammetry. A brief summary of these investigations are also reported at the end of this part which is followed by important references.