PREFACE

Schiff bases are a class of compounds which have profound use as ligands as well as in the form of complexes. The versatile use of Schiff bases is due to its ability to coordinate to the metal ions via the azomethine nitrogen. Schiff bases are useful chelators because of their ease of preparation and structural varieties. Multidentate Schiff base ligands and their coordination with metals attract much attention because of their biological relevance. Heterocyclic Schiff bases have wide application in therapeutic fields either as potential drug or diagnostic probes and also in analytical tools. The presence of hetero atoms in such ligands gives them excellent characteristics like corrosion inhibition property. During the present course of study five monovalent Schiff base ligands and their transition metal complexes were prepared and characterized. Antitumour studies of the copper complexes of all these Schiff bases were conducted. Investigations of the corrosion inhibition capacity of the newly synthesized Schiff bases have been carried out in different acid media. Thermoanalytical studies of some of the complexes were also conducted. For convenience and better understanding, the entire work has been presented in this thesis as four parts.

In the first part of the thesis, five novel heterocyclic Schiff bases namely 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA), (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA), (E)-4-(5-[(2-carbamo thioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) were synthesized and characterized by different techniques like CHNS analysis and spectral

studies such as FTIR, NMR, mass and UV-visible. The chelating abilities of these Schiff bases were investigated by synthesizing a number of transition metal complexes. Elemental analysis shows that majority of the metal complexes obey 1:1 stoichiometry between the metal and ligand. Out of the five studied Schiff bases, majority of them acted as monovalent bidentate ligands in metal complexes, coordinating through azomethine nitrogen and carboxylate oxygen. Then these complexes were also subjected to characterization studies by elemental analysis, magnetic moment measurements, conductance measurements, IR, UV-visible and ^{1}Hnmr spectral analysis.

This part is divided into seven chapters. The first chapter includes details of literature survey and the scope of present investigation. Various physicochemical methods employed for the elucidation of the structures of the Schiff bases and their metal chelates are discussed in chapter 2. Details of synthesis and characterization of Schiff bases, 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA), (E)-3-[thiophen -2-ylmethyleneamino]benzoic acid (T2YMABA), (E)-4-(5-[(2-carbamothioylhydrazono) methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), (E)-4-(5-[(2-phenylhydrazono) methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioyl hydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) and their transition metal complexes are presented in the chapters 3, 4, 5, 6 and 7 respectively. This part ends with a brief summary and references.

Thermogravimetric studies of Cr(III) and Ni(II) complexes of novel Schiff base ligands such as I3YT2YMAPA, T2YMABA, CTHMT2YBA, PHMT2YBA and CTHMF2YBA are given in Part II. The regions of thermal stability and the temperature of decomposition of each of these complexes were found out. Also the temperatures of

maximum rate of decomposition were assigned from the thermograms. Kinetic studies were done based on these thermogravimetric data by employing mechanistic and non mechanistic equations. Kinetic parameters like Arrhenius frequency factor, energy of activation and entropy of activation of all the decomposition stages were calculated. The mechanism of decomposition reaction in each stage and hence the order of decomposition reactions also were determined. The thermal stabilities of the chelates were compared with the aid of energy of activation, initial/final decomposition temperature, inflection temperature and peak temperature from the TG and DTA data. In order to ascertain the order of the decomposition reactions, nine mechanistic equations and an integral equation formulated by Coats and Redfern, which is a non mechanistic equation, were employed. Comparing the correlation between the kinetic parameters obtained from these mechanistic equations and the Coats-Redfern method, reaction mechanisms and orders of different decomposition stages were ascertained.

First chapter of this part involves an introduction on different thermoanalytical methods like TGA and DTA. The relevance of various methods for the determination of kinetic parameters of solid-state reactions using thermogravimetric data, especially the Coats-Redfern method is discussed here. The scope of present studies is also mentioned. Details of the instruments used are given in chapter 2. The thermal decomposition data and the evaluation of kinetic parameters of Cr(III) complexes of the Schiff bases, T2YMABA, PHMT2YBA, CTHMT2YBA and CTHMF2YBA are discussed obviously and reported in chapter 3. Whereas in chapter 4, the thermal behaviour and kinetic studies of Ni(II) complexes of T2YMABA, PHMT2YBA, CTHMT2YBA, CTHMF2YBA and

I3YT2YMAPA are explained. All the results are briefly summarized at the end of this part followed by references.

Part III deals with the detailed investigations of the corrosion inhibition capacity of the newly synthesized Schiff bases on mild steel in hydrochloric acid and sulphuric acid media. The corrosion inhibition studies were carried out with conventional gravimetric method and electrochemical methods such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies. In the polarization analysis, Tafel extrapolation method and Linear polarization method were performed separately. Both Nyquist plot and Bode plot analysis were utilized to get much density on the inhibitory action of the novel Schiff bases by EIS method. Adsorption isotherms were plotted from the results of gravimetric weight loss studies in order to predict the mechanism of corrosion inhibition by the Schiff bases. Thermodynamic parameters like free energy of adsorption and adsorption equilibrium constant were also determined for confirming the nature of adsorption. Weight loss method was followed to compare the inhibition efficiencies of Schiff bases and their respective parent amines in acid medium. Corrosion studies clearly established that all the studied Schiff bases were excellent corrosion inhibitors on mild steel in hydrochloric acid medium. Generally the corrosion inhibition efficiency was poor in H_2SO_4 medium than in HCl medium. Surface morphological analysis was also conducted to establish the mechanism of corrosion inhibition of these inhibitors.

This part is comprised of three chapters, whereas the third chapter consists of two subsections. Chapter 1 details the different aspects of corrosion and corrosion inhibitors. A report of thorough literature survey on corrosion inhibition studies and the scope of the

present study are also included in this chapter. The details of different corrosion monitoring techniques are discussed in chapter 2. Results and discussion of corrosion inhibition investigations of the newly synthesized Schiff bases in different acid media have been reported well in chapter 3. This chapter is divided into two sections; In section I corrosion inhibition studies of Schiff base inhibitors on mild steel in 1.0 M HCl is given and in Section II, the studies in 0.5M H_2SO_4 medium are detailed. A brief summary of the corrosion studies along with the references are followed thereafter.

The details of antitumour studies are explained well in Part IV of this thesis. The antitumour activity of copper(II) complexes of ten different potential Schiff base ligands such as 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA), (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA), (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA), 2-(1-[pyridin-3-yl]ethylidene)hydrazinecarbothioamide (P3YEHCTA), 3-(1-[2-phenyl hydrazono]ethyl)pyridine (PHEP), 3-[anthracen-9(10H)-ylideneamino]propanoic acid (A9Y3APA), 2-[anthracen-9(10H)-ylideneamino]-3-(1H–imidazole–4-yl)propanoic acid (A9Y3IMPA) and 2-[anthracen-9(10H)-ylideneamino]-3-phenylpropanoic acid (A9Y3PPA) were examined on Dalton's lymphoma ascites tumour cells. Firstly, Cu(II) complexes of these Schiff bases were prepared and screened for their *in vitro* cytotoxic activity. The trypan blue exclusion method was adopted and the results revealed that all the complexes have excellent cytotoxic activity against the tumour cell suspension. Three complexes which showed the highest activity during *in vitro* cytotoxic analysis were

chosen for the *in vivo* studies on Swiss albino mice. Ascites tumour reduction analysis explored the increased capacity of the copper compounds on chelation. Also the activities of these compounds were compared with that of the standard drug cyclophosphamide.

Chapter 1 of this part includes an elaborate introduction on different types of tumour and the details of earlier antitumour investigations. Objectives and scope of the investigation are also given in this chapter. Chapter 2 includes different strategies adopted for studying the inhibitory effect of copper complexes of various Schiff bases. Results and discussion of the antitumour studies of various Schiff base complexes are portrayed in chapter 3. This part terminates with the summary and bibliography.