

SINI VARGHESE C. “ EVALUATION ON THE INHIBITIVE EFFECT OF HETEROCYCLIC DERIVATIVES AND POLYAMINO COMPOUNDS ON THE CORROSION OF CARBON STEEL AND COPPER IN ACID MEDIA.” THESIS. RESEARCH AND POSTGRADUATE DEPARTMENT OF CHEMISTRY, ST. THOMAS’ COLLEGE (AUTONOMOUS), UNIVERSITY OF CALICUT, 2019.

## **DECLARATION**

I hereby declare that the thesis entitled “**Evaluation on the Inhibitive Effect of Heterocyclic Derivatives and Polyamino Compounds on the Corrosion of Carbon Steel and Copper in Acid Media**”, submitted to the University of Calicut in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry is a bonafide research work done by me under the supervision and guidance of Dr. Joby Thomas. K, Associate Professor and Head, Department of Chemistry, St. Thomas’ College, Thrissur.

I further declare that this thesis has not previously formed the basis of any degree, diploma or any other similar title.

**Sini Varghese C**

## **ACKNOWLEDGEMENTS**

*I devote this thesis at the feet of God Almighty whose invisible presence guided me through each step of my journey towards the fulfillment of my ambition.*

*I sincerely acknowledge my guide and my mentor Dr. Joby Thomas K, without whose selfless commitment and motivation I could not have completed this humble venture. I would also cherish this experience in the rest of my life as I am really lucky to work under a pioneer in the field of Chemistry.*

*My dream would have been impossible without the incessant co-operation, love and encouragement from my family members.*

*I am grateful to Dr. Joy K. L, Principal, Dr. Ignatius Antony and Dr. P. O Jenson, former Principals, all the faculty members of Chemistry Department, especially former Heads of Department, Dr. Joy Anto and Dr. Babu Joseph, Lab Assistants and Office staffs, for the invaluable support they offered whenever I was in need.*

*I hereby express my extreme gratitude for the moral support and encouragement given by my seniors Dr. Vinod P. Rapheal, Dr. Shaju K. S, Dr. Nimmy Kuriakose and Dr. Aby Paul, especially the advice given by Dr. Vinod P. Rapheal helped me a lot in doing the corrosion inhibition studies by protective coatings.*

*I am grateful to my fellow scholars Binsi, Reeja, Dinoop, Ragi, Drishya, Vidhya, Ramesh, Aji, Rohini, Anju, Swathy, Nithya, Neera, Siji, Memsy, Martin, Savitha, Raji, and Sr. Jisha, who helped me a lot in completing this research.*

*I recollect the blessings and support from the faculty members, Dept. of Chemistry, St Josephs' College Irinjalakuda. I also recall with gratitude the support and the motivation rendered by my dear friends especially Fredy.*

*I hereby acknowledge the help rendered by the STIC-CUSAT, NIT Calicut and Mr. Vishnu of IISER Trivandrum in analyzing the compounds. I also thank Mr. M. I. Pauly, Educare, Thrissur, who did the entire printing work of my thesis.*

***Sini Varghese C***

*To*  
*My Family*

---

## PREFACE

Heterocyclic chemistry is a very important branch of organic chemistry which deals with the synthesis, characterization and application of these heterocyclic compounds. Two third of the organic compounds discovered so far are heterocyclic compounds and the presence of the hetero atoms makes them quite distinct from other molecules in terms of activity and reactivity. They are used as starting materials and reagents in synthesizing a variety of organic compounds which are synthetic intermediates, protecting groups, chiral auxiliaries, organic catalysts and organo-metallic ligands. They have a wide variety of uses including polymeric, supramolecular materials, dyestuffs, fluorescent sensors, brightening agents, information storage, plastics, analytical reagents, developers, sensitizers, antioxidants, corrosion inhibitors and even as rocket propellants. One of the major applications for the heterocyclic compounds is in the field of corrosion prevention.

Imines are organic compounds formed when a primary amine reacts with an aldehyde or ketone and are analogous to aldehydes and ketones in the sense they have a C=N in the place of a C=O bond. Heterocyclic imines are an important class of heterocyclic derivatives. A wide range of contexts were checked out for their useful applications including catalysis, corrosion protection, antimicrobial, antiviral and anti-cancer activities. The application of imines as corrosion inhibitors is based on their ability to form a monolayer over the surface to be protected. Their corrosion prevention properties are attributed to the

presence of azomethine moiety, electron cloud on aromatic ring and the electronegative atoms which can be incorporated in the molecules like oxygen, sulphur and nitrogen. The metal corrosion is an important threat which can affect directly or indirectly on the economy, so the study of the heterocyclic imines as corrosion inhibitors was considered as foremost research area to prevent the metal deterioration. During the present course of study seven heterocyclic imines from pyridine carbaldehyde and four imines from 3-formylindole carbaldehyde were prepared and characterized. Investigations of the corrosion inhibition properties of the newly synthesized heterocyclic imines have been carried out on carbon steel and copper in different acid media.

Scientists and researchers are ever in searching for novel and effective methods to minimize the corrosion. Out of various methods to combat against corrosion is to make protective coatings on the metallic substrates. To find out an effective, durable and protective coating is a thrust area of research in the field of corrosion protection. Apart from the conventional coatings using paints, oils, varnishes etc, nowadays scientist rely upon special type of polymeric coatings. Polymeric anticorrosive coatings are mainly done by electrochemical methods. Electrodeposition is the most convenient way to make protective coatings using conducting polymers to reduce the metallic corrosion. For convenience and better understanding the entire work has been presented in this thesis as three parts.

In the first part of the thesis, seven heterocyclic imines, derived from pyridine carbaldehyde such as pyridine-2-carbaldehyde oxime, 2PCOX [or *N*-hydroxy-1-(pyridin-2-yl)methanimine], pyridine-3-carbaldehyde oxime, 3PCOX

[or *N*-hydroxy-1-(pyridin-3-yl)methanimine], pyridine-2-carbaldehyde-4-aminobenzoic acid, 2PC4ABA [or 4-(pyridin-2-ylmethyleneamino)benzoic acid], pyridine-2-carbaldehyde-3-aminobenzoic acid, 2PC3ABA [or 3-(pyridin-2-ylmethyleneamino)benzoic acid], pyridine-2-carbaldehyde-2-aminobenzoic acid, 2PC2ABA [or 2-(pyridin-2-ylmethyleneamino)benzoic acid], pyridine-3-carbaldehyde-3-aminobenzoic acid, 3PC3ABA [or 3-(pyridin-3-ylmethyleneamino)benzoic acid] and pyridine-2-carbaldehyde-2-aminophenol, 2PC2AP [or 2-(pyridin-2-ylmethyleneamino)phenol] and the four imine compounds from 3-formylindole carbaldehyde namely 3-formylindole phenylhydrazone, 3FIPH [or 3-((2-phenylhydrazono)methyl)-1H-indole], 3-formylindole semicarbazone 3FISC [or 2-((1H-indol-3-yl)methylene)hydrazinecarboxamide], 3-formylindole thiosemicarbazone, 3FITSC (or 2-((1H-indol-3-yl)methylene)hydrazinecarbothioamide] and 3-formylindole-1,2-diaminocyclohexane, 3FIDACH [or  $N^1,N^2$ -bis((1H-indol-3-yl)methylene)cyclohexane-1,2-diamine] were synthesized. Various physicochemical investigations have been performed to elucidate their structures. The analytical tools employed are CHN analysis and spectral studies such as FTIR, UV-visible, Mass  $^1\text{Hnmr}$ ,  $^{13}\text{Cnmr}$ , and DEPT. The elemental analysis showed that 1:1 stoichiometry exist between the aldehyde and amine in majority of the imines, while only 3FIDACH showed 2:1 stoichiometry. This part is divided into four chapters.

The chapter 1 consists of an introduction to heterocyclic compounds, applications of heterocyclic compounds, heterocyclic imine compounds and a

thorough review of published work on heterocyclic compounds, nitrogen containing heterocyclic derivatives and heterocyclic imines as corrosion inhibitors. Scope and objectives of the present study are also given here. Various physicochemical methods employed for the elucidation of the structure of imines are discussed in Chapter 2. The methods used are CHN analysis and spectral studies such as FTIR, UV-visible,  $^1\text{Hnmr}$ ,  $^{13}\text{Cnmr}$ , DEPT and Mass spectroscopy. The Chapter 3 includes the details of synthesis and characterization of seven heterocyclic imines 2PCOX, 3PCOX, 2PC4ABA, 2PC3ABA, 2PC2ABA, 3PC3ABA and 2PC2AP derived from pyridine carbaldehyde. The synthesis and characterization of four heterocyclic imines 3FIPH, 3FISC, 3FITSC and 3FIDACH derived from 3- formylindole carbaldehyde were described in Chapter 4. At the end of this part a brief summary of the synthetic and physicochemical evaluations of all studied imines are presented followed by a wide spectrum of bibliography.

Part II deals with the detailed investigations of corrosion inhibition studies of the synthesized heterocyclic imines on carbon steel in hydrochloric acid and sulphuric acid media and copper in nitric acid medium. The corrosion inhibition studies were conducted by conventional gravimetric studies and electrochemical analyses, such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization technique and electrochemical noise measurement. To predict the mechanism of corrosion inhibition of the imines, adsorption isotherms were plotted and were verified by surface morphological studies (using SEM analysis). In order to determine the 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. Inhibition efficiencies of heterocyclic imines are compared with their respective parent amines by gravimetric studies. The quantum mechanical investigations were also conducted to correlate the inhibition efficiency of heterocyclic imines theoretically and experimentally. The optimized geometry, HOMO and LUMO molecular orbitals are also obtained from quantum mechanical studies. This part is divided into five chapters and the chapters 3, 4 and 5 have been sub-divided into two subsections each.

The chapter 1 deals with detailed description of corrosion, types of corrosion, corrosion related problems in various industries, it's after effects, corrosion prevention methods and corrosion inhibitors. Review of literature and scope of this study with newly synthesized heterocyclic imine are also documented here. The experimental details of different corrosion monitoring techniques are depicted in chapter 2. The chapter 3 contains corrosion inhibition studies of heterocyclic imines on carbon steel in 1.0M HCl. This chapter is divided into two subsections. Corrosion inhibition studies of heterocyclic imines derived from pyridine carbaldehyde such as 2PCOX, 3PCOX, 2PC4ABA, 2PC3ABA, 2PC2ABA, 3PC3ABA and 2PC2AP on carbon steel in 1.0M HCl are described in section I. In section II corrosion inhibition studies of heterocyclic imines derived from 3-formylindole carbaldehyde namely 3FIPH, 3FISC, 3FITSC and 3FIDACH on carbon steel in 1.0M HCl are well documented.

The corrosion inhibition studies of heterocyclic imines on carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> are described in chapter 4, and this chapter is also subdivided into two sections. Corrosion inhibition studies of heterocyclic imines derived from pyridine carbaldehyde on carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> are well portrayed in the first section. The detailed picture of corrosion inhibition analysis of heterocyclic imines derived from 3-formylindole carbaldehyde on carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> is included in section II. The description on anticorrosive properties of heterocyclic imines on copper in 0.1M HNO<sub>3</sub> are narrated in chapter 5 with two subsections. The section I deal with the corrosion inhibition studies of heterocyclic imines derived from pyridine carbaldehyde on copper in 0.1M HNO<sub>3</sub>. In section II emphasis is given for the corrosion inhibition studies of heterocyclic imines derived from 3-formylindole carbaldehyde on copper in 0.1M HNO<sub>3</sub>. A brief summary of the corrosion inhibition studies of heterocyclic imines derived, is followed thereafter along with relevant references.

In part III, seven amino compounds such as polyaniline [PANI], poly(2-aminobenzoic acid) [P2ABA], poly(3-aminobenzoic acid) [P3ABA], poly(2-aminobenzene sulphonic acid) [P2ABSA], poly(2-nitroaniline) [P2NA], poly(3-nitroaniline) [P3NA] and poly(2-aminophenol) [P2AP] were electrochemically polymerized in HCl medium using cyclic voltammetry. During the electrochemical process, the synthesized polymers were coated on the surface of the working electrode. Carbon steel specimen was used as the working electrode in cyclic voltammetry. The coated polymers were tested for their corrosion protection capacity in 1.0M HCl solution at two different conditions. The coated

samples were dried, exposed to air for 24hours and then immersed in the aggressive medium for performing electrochemical analysis such as Tafel and EIS studies. Secondly the coated specimens were directly immersed in 1.0M HCl for 24hours and conducted Tafel and EIS studies. The structural characteristics of the electrochemically synthesized polymers were compared with the structural behaviour of the chemically synthesized polymers using FTIR technique. To explain the mechanism of corrosion protection, surface morphological analysis was also done using scanning electron microscopy. This part is divided into three chapters.

The first chapter consists of an introduction to polymeric coating on metals and a detailed survey of published work on polymeric coating on metals to prevent the corrosion. Scope and objectives of the present study are also included here. Various physicochemical, electrochemical and surface analysis methods used for the investigation of corrosion inhibition efficiency of polyamino compounds are explained in chapter 2. Detailed investigations on protective polymeric coatings by PANI, P2ABA, P3ABA, P2ABSA, P2NA, P3NA and P2AP, employing electrochemical methods such as Tafel and EIS studies are well depicted in chapter 3. FTIR and SEM analysis were also performed to study the surface phenomena. A brief summary of these investigations are also reported at the end of this part which is followed by bibliography.

## ABBREVIATIONS

2PCOX	Pyridine-2-carbaldehyde oxime
3PCOX	Pyridine-3-carbaldehyde oxime
2PC4ABA	Pyridine-2-carbaldehyde -4-aminobenzoic acid
2PC3ABA	Pyridine-2-carbaldehyde -3-aminobenzoic acid
2PC2ABA	Pyridine-2-carbaldehyde -2-aminobenzoic acid
3PC3ABA	Pyridine-3-carbaldehyde -3-aminobenzoic acid
2PC2AP	Pyridine-2-carbaldehyde -2-aminophenol
3FIPH	3-formylindole phenylhydrazone
3FISC	3-formylindole semicarbazone
3FITSC	3-formylindole thiosemicarbazone
3FIDACH	3-formylindole-1, 2-diaminocyclohexane
ppm	Parts per million
CS	Carbon Steel
EIS	Electrochemical Impedance Spectroscopy
DMSO	Dimethyl Sulphoxide
CV	Cyclic Voltammetry
PANI	Polyaniline
P2ABA	Poly(2-aminobenzoic acid)
P3ABA	Poly(3-aminobenzoic acid)
P2ABSA	Poly(2-aminobenzene sulphonic acid)
P2NA	Poly(2-nitroaniline)
P3NA	Poly(3-nitroaniline)
P2AP	Poly(2-aminophenol)

## ABSTRACT

Heterocyclic chemistry is a very important branch of organic chemistry which deals with the synthesis, characterization and application of heterocyclic compounds. Heterocyclic imines had wide range of applications in catalysis, corrosion protection and biological fields. One of the major applications of the heterocyclic imines is in the field of corrosion prevention. Their anticorrosive properties are attributed to the presence of azomethine moiety, electron cloud on aromatic ring and the electronegative atoms which can be incorporated in the molecules like oxygen, sulphur and nitrogen. Scientists and researchers are ever in searching for novel and effective methods to minimize the corrosion. One of the prominent methods to combat against corrosion is to make protective coatings on the metallic substrates. Electrodeposition, using conducting polymers is the most convenient way to make protective coatings.

In this thesis, potential heterocyclic imines were synthesized and characterized. The corrosion inhibition studies of these imines were conducted. The investigations on the efficiency of some polymeric coatings using polyamino compounds on carbon steel corrosion were also established. The entire work is presented in this thesis as three parts. In the first part, synthesis and characterization of eleven heterocyclic imines derived from pyridine-2-carbaldehyde and 3-formylindole carbaldehyde were discussed. The synthetic routes to these molecules were explained and characterized them by various methods, such as CHN analysis, NMR, Mass, IR and UV-visible spectroscopic studies. Except one, all the imines satisfied 1:1 aldehyde and amine stoichiometry.

Part II contains the corrosion inhibition studies of these synthesized heterocyclic imines on carbon steel in HCl as well as H<sub>2</sub>SO<sub>4</sub> media and also on copper in HNO<sub>3</sub> medium. The corrosion inhibition studies were performed by weight loss studies, electrochemical studies, such as electrochemical impedance spectroscopy, potentiodynamic polarization technique and noise measurement. Temperature studies were performed in the range 30-60<sup>0</sup>C. Adsorption isotherms were plotted and surface morphological studies were performed using SEM to predict the mechanism of inhibition. Quantum mechanical investigations using GAMMESS software were established. Generally all the heterocyclic imines showed very good corrosion inhibition efficiency on carbon steel in HCl, as well as copper in HNO<sub>3</sub> media. Relatively poor inhibition efficacy was exhibited by these imines in H<sub>2</sub>SO<sub>4</sub> medium.

The corrosion inhibition studies of protective coatings on carbon steel are explained in part III. Seven amino compounds were electrochemically polymerized in HCl medium using cyclic voltammetry. The coated polymers were tested for their corrosion protection capacity in 1.0M HCl solution at two different conditions, using Tafel and EIS studies. The structural characteristics of the electrochemically synthesized polymers were compared with the chemically synthesized polymers using FTIR technique and SEM analysis was employed to study the surface morphology. Generally the studied polymeric coatings were found to have excellent corrosion inhibition efficiency towards carbon steel corrosion in HCl medium.

## LIST OF CONTENTS

<b>PART I</b>		
<b>SYNTHESIS AND CHARACTERIZATION</b>		
<b>CHAPTER 1</b>	INTRODUCTION AND REVIEW	1
	Heterocyclic compounds	1
	Classification of heterocyclic compounds	2
	Importance of heterocyclic compounds	4
	Heterocyclic compounds as corrosion inhibitors	8
	Nitrogen heterocyclic derivatives as corrosion inhibitors	12
	Heterocyclic derivatives: imines	17
	Applications of imines	20
	Imine compounds as corrosion inhibitors	22
	Imines with nitrogen heterocycles as corrosion inhibitors	25
	Scope and objectives of the present investigation	28
<b>CHAPTER 2</b>	MATERIALS AND METHODS	30
<b>CHAPTER 3</b>	STUDIES ON HETEROCYCLIC IMINES DERIVED FROM PYRIDINE CARBALDEHYDE	33
	Synthesis and characterization of the heterocyclic imine: <i>N</i> -hydroxy-1-(pyridin-2-yl)methanimine	33
	Synthesis and characterization of the heterocyclic imine: <i>N</i> -hydroxy-1-(pyridin-3-yl)methanimine	38
	Synthesis and characterization of the heterocyclic imine: 4-(pyridin-2-ylmethyleneamino)benzoic acid	42
	Synthesis and characterization of the heterocyclic imine: 3-(pyridin-2-ylmethyleneamino)benzoic acid	47
	Synthesis and characterization of the heterocyclic imine: 2-(pyridin-2-ylmethyleneamino)benzoic acid	51
	Synthesis and characterization of the heterocyclic imine: 3-(pyridin-3-ylmethyleneamino)benzoic acid	55
	Synthesis and characterization of heterocyclic imine: 2-(pyridin-2-ylmethyleneamino)phenol	59
<b>CHAPTER 4</b>	STUDIES ON HETEROCYCLIC IMINES DERIVED FROM 3-FORMYLINDOLE CARBALDEHYDE	63
	Synthesis and characterization of the heterocyclic imine: 3-((2-phenylhydrazono)methyl)-1H-indole	63
	Synthesis and characterization of the heterocyclic imine: 2-((1H-indol-3-yl)methylene) hydrazine carboxamide	68
	Synthesis and characterization of the heterocyclic imine: 2-((1H-indol-3-yl)methylene)hydrazinecarbo thioamide	72

	Synthesis and characterization of the heterocyclic imine: N <sup>1</sup> , N <sup>2</sup> -bis((1H-indol-3-yl)methylene)cyclohexane -1,2-diamine	75
	SUMMARY	81
	REFERENCES	84
<b>PART II</b>		
<b>CORROSION INHIBITION STUDIES</b>		
<b>CHAPTER 1</b>	INTRODUCTION AND REVIEW	93
	Corrosion	93
	Corrosion: Consequences	94
	Different types of corrosion	99
	Corrosion control by inhibitors	105
	Review on organic inhibitors on steel in acidic media	110
	Copper corrosion	120
	Review on organic inhibitors on copper in acidic media	122
	Scope and objectives of the present investigation	126
<b>CHAPTER 2</b>	MATERIALS AND METHODS	128
<b>CHAPTER 3</b>	CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES ON CARBON STEEL IN 1.0M HCl	148
<b>SECTION I</b>	CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES DERIVED FROM PYRIDINE CARBALDEHYDE ON CARBON STEEL IN 1.0M HCl	149
	Weight loss studies	149
	Comparison between the inhibition efficiency of imines and its parent amines	154
	Adsorption studies	156
	Temperature studies	159
	Electrochemical impedance spectroscopy (EIS) studies	165
	Potentiodynamic polarization studies	171
	Electrochemical noise studies	176
	Quantum mechanical studies	180
Surface morphological studies	186	
<b>SECTION II</b>	CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES DERIVED FROM 3-FORMYLINDOLE CARBALDEHYDE ON CARBON STEEL IN 1.0M HCl	187
	Weight loss Studies	187
	Comparison between the inhibition efficiency of imines and its parent amines	191
	Adsorption studies	192
	Electrochemical impedance spectroscopy (EIS) studies	194
	Potentiodynamic polarization studies	198
	Electrochemical noise studies	203



	Quantum mechanical studies	206
	Surface morphological studies	209
<b>CHAPTER 4</b>	<b>CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES ON CARBON STEEL IN 0.5M H<sub>2</sub>SO<sub>4</sub></b>	211
<b>SECTION I</b>	<b>CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES DERIVED FROM PYRIDINE CARBALDEHYDE ON CARBON STEEL IN 0.5M H<sub>2</sub>SO<sub>4</sub></b>	212
	Weight loss studies	212
	Adsorption studies	214
	Electrochemical impedance spectroscopy (EIS) studies	218
	Potentiodynamic polarization studies	223
	Surface morphological studies	228
<b>SECTION II</b>	<b>CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES DERIVED FROM 3-FORMYLINDOLE CARBALDEHYDE ON CARBON STEEL IN 0.5M H<sub>2</sub>SO<sub>4</sub></b>	230
	Weight loss studies	230
	Adsorption studies	233
	Electrochemical impedance spectroscopy (EIS) studies	235
	Potentiodynamic polarization studies	240
	Surface morphological studies	244
<b>CHAPTER 5</b>	<b>CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES ON COPPER IN 0.1M HNO<sub>3</sub></b>	246
<b>SECTION I</b>	<b>CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES DERIVED FROM PYRIDINE CARBALDEHYDE ON COPPER IN 0.1M HNO<sub>3</sub></b>	247
	Electrochemical impedance spectroscopy (EIS) studies	248
	Adsorption studies	256
	Potentiodynamic polarization studies	260
	Quantum mechanical studies	265
	Surface morphological studies	267
<b>SECTION II</b>	<b>CORROSION INHIBITION STUDIES OF HETEROCYCLIC IMINES DERIVED FROM 3-FORMYLINDOLE CARBALDEHYDE ON COPPER IN 0.1M HNO<sub>3</sub></b>	269
	Electrochemical impedance spectroscopy (EIS) studies	269
	Adsorption studies	273
	Potentiodynamic polarization studies	275
	Quantum mechanical studies	279
	Surface morphological studies	280
	<b>SUMMARY</b>	282

	REFERENCES	287
<b>PART III</b>		
<b>CORROSION INHIBITION BY PROTECTIVE COATINGS</b>		
<b>CHAPTER 1</b>	INTRODUCTION AND REVIEW	296
	Methods of polymerization	298
	Review on corrosion inhibition by protective coatings	300
	Scope and objectives of the present investigation	305
<b>CHAPTER 2</b>	<b>MATERIALS AND METHODS</b>	307
<b>CHAPTER 3</b>	CORROSION INHIBITION STUDIES OF POLYAMINO COMPOUNDS AS PROTECTIVE COATINGS ON CARBON STEEL IN 1.0M HCl	311
	Electrochemical impedance spectroscopy (EIS) studies	315
	Potentiodynamic polarization studies	325
	IR spectral studies	331
	Surface morphological studies	334
	SUMMARY	336
	REFERENCES	338

## LIST OF TABLES

Table No.	Title	Page No.
<b>PART I SYNTHESIS AND CHARACTERIZATION</b>		
1.1	Microanalytical and spectral data of 2PCOX	34
1.2	Microanalytical and spectral data of 3PCOX	38
1.3	Microanalytical and spectral data of 2PC4ABA	44
1.4	Microanalytical and spectral data of 2PC3ABA	49
1.5	Microanalytical and spectral data of 2PC2ABA	51
1.6	Microanalytical and spectral data of 3PC3ABA	56
1.7	Microanalytical and spectral data of 2PC2AP	61
1.8	Microanalytical and spectral data of 3FIPH	64
1.9	Microanalytical and spectral data of 3FISC	70
1.10	Microanalytical and spectral data of 3FITSC	72
1.11	Microanalytical and spectral data of 3FIDACH	77
<b>PART II CORROSION INHIBITION STUDIES</b>		
2.1	Corrosion rate of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 1.0M HCl	150
2.2	Corrosion inhibition efficiencies of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl.	151
2.3	Corrosion inhibition efficiencies of heterocyclic imines of pyridine carbaldehyde and their parent amines on CS in 1.0M HCl.	155
2.4	Adsorption isotherms and regression coefficients of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl	156
2.5	Adsorption parameters of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl	159
2.6	Thermodynamic parameters of corrosion of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 1.0M HCl.	162
2.7	Electrochemical impedance parameters of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 1.0M HCl	166
2.8	Potentiodynamic polarization parameters of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 1.0M HCl	175
2.9	Quantum mechanical parameters of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl	181
2.10	Corrosion rate of CS in the presence and absence of heterocyclic imines of 3-formylindole carbaldehyde in 1.0M HCl	188
2.11	Inhibition efficiencies of heterocyclic imines of 3-formyl indole carbaldehyde on CS in 1.0M HCl	189

2.12	Corrosion inhibition efficiencies of heterocyclic imines of 3-formylindole carbaldehyde and their parent amines on CS in 1.0M HCl	191
2.13	Adsorption isotherms and the regression coefficient of heterocyclic imines of 3-formylindole carbaldehyde on CS in 1.0M HCl	192
2.14	Adsorption parameters of heterocyclic imines of 3-formyl indole carbaldehyde on CS in 1.0M HCl	193
2.15	Electrochemical impedance parameters of CS in the presence and absence of heterocyclic imines of 3-formyl indole carbaldehyde in 1.0M HCl	195
2.16	Potentiodynamic polarization parameters of CS in the presence and absence of heterocyclic imines of 3-formyl indole carbaldehyde in 1.0M HCl	201
2.17	Quantum mechanical parameters of heterocyclic imines of 3-formylindole carbaldehyde on CS in 1.0M HCl	207
2.18	Corrosion rate of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 0.5M H <sub>2</sub> SO <sub>4</sub>	213
2.19	Corrosion inhibition efficiencies of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	214
2.20	Adsorption isotherms and the regression coefficients of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	215
2.21	Adsorption parameters of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	215
2.22	Electrochemical impedance parameters of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 0.5M H <sub>2</sub> SO <sub>4</sub>	219
2.23	Potentiodynamic polarization parameters of CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 0.5M H <sub>2</sub> SO <sub>4</sub>	225
2.24	Corrosion rate of CS in the presence and absence of heterocyclic imines of 3-formylindole carbaldehyde in 0.5M H <sub>2</sub> SO <sub>4</sub>	231
2.25	Inhibition efficiencies of heterocyclic imines of 3-formyl indole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	232
2.26	Adsorption isotherms and regression coefficients of heterocyclic imines of 3-formylindole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	233
2.27	Adsorption parameters of heterocyclic imines of 3-formylindole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	233
2.28	Electrochemical impedance parameters of CS in the presence and absence of heterocyclic imines of 3-formyl indole carbaldehyde in 0.5M H <sub>2</sub> SO <sub>4</sub>	237
2.29	Potentiodynamic polarization parameters of CS in the presence and absence of heterocyclic imines of 3-formyl indole carbaldehyde in 0.5M H <sub>2</sub> SO <sub>4</sub>	242

2.30	Electrochemical impedance parameters of copper in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 0.1M HNO <sub>3</sub>	252
2.31	Adsorption isotherms and the regression coefficients of heterocyclic imines of pyridine carbaldehyde on copper in 0.1M HNO <sub>3</sub>	256
2.32	Adsorption parameters of heterocyclic imines of pyridine carbaldehyde on copper in 0.1M HNO <sub>3</sub>	259
2.33	Potentiodynamic polarization parameters of copper in the presence and absence of heterocyclic imines of pyridine carbaldehyde in 0.1M HNO <sub>3</sub>	263
2.34	Quantum mechanical parameters of heterocyclic imines of pyridine carbaldehyde on copper in 0.1M HNO <sub>3</sub>	267
2.35	Electrochemical impedance parameters of copper in the presence and absence of heterocyclic imines of 3-formyl indole carbaldehyde in 0.1M HNO <sub>3</sub>	272
2.36	Adsorption isotherms and the regression coefficients of heterocyclic imines of 3-formylindole carbaldehyde on copper in 0.1M HNO <sub>3</sub>	274
2.37	Adsorption parameters of heterocyclic imines of 3-formylindole carbaldehyde on copper in 0.1M HNO <sub>3</sub>	274
2.38	Potentiodynamic polarization parameters of copper in the presence and absence of heterocyclic imines of 3-formyl indole carbaldehyde in 0.1M HNO <sub>3</sub>	278
2.39	Quantum mechanical parameters of heterocyclic imines of 3-formylindole carbaldehyde on copper in 0.1M HNO <sub>3</sub>	280
<b>PART III CORROSION INHIBITION BY PROTECTIVE COATINGS</b>		
3.1	Name, abbreviation and skeletal structures of electrochemically synthesized polyamino compounds	312
3.2	Electrochemical impedance parameters of CS specimens coated with polyamino compounds kept for 24h in air and treated with 1.0M HCl	316
3.3	Electrochemical impedance parameters of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h	316
3.4	Tafel data of CS specimens coated with polyamino compounds kept for 24h in air and treated with 1.0M HCl	326
3.5	Tafel data of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h	326
3.6	Type of corrosion inhibition by polyamino compounds on CS specimen in 1.0M HCl in condition 1	330
3.7	Characteristic IR frequencies of chemically and electrochemically synthesized polyamino compounds	333

## LIST OF FIGURES

Figure No.	Title	Page No.
<b>PART I SYNTHESIS AND CHARACTERIZATION</b>		
1.1	<sup>1</sup> Hnmr spectrum of imine 2PCOX	35
1.2	<sup>13</sup> Cnmr spectrum of imine 2PCOX	35
1.3	Mass spectrum of imine 2PCOX	36
1.4	Structure of 2PCOX	37
1.5	<sup>1</sup> Hnmr spectrum of imine 3PCOX	39
1.6	<sup>13</sup> Cnmr spectrum of imine 3PCOX	40
1.7	Mass spectrum of imine 3PCOX	40
1.8	Structure of 3PCOX	41
1.9	<sup>1</sup> Hnmr spectrum of imine 2PC4ABA	43
1.10	<sup>13</sup> Cnmr spectrum of imine 2PC4ABA	43
1.11	Mass spectrum of imine 2PC4ABA	45
1.12	Structure of 2PC4ABA	46
1.13	<sup>1</sup> Hnmr spectrum of imine of 2PC3ABA	48
1.14	<sup>13</sup> Cnmr spectrum of imine 2PC3ABA	48
1.15	Mass spectrum of imine 2PC3ABA	49
1.16	Structure of 2PC3ABA	50
1.17	<sup>1</sup> Hnmr spectrum of imine 2PC2ABA	52
1.18	<sup>13</sup> Cnmr spectrum of imine 2PC2ABA	53
1.19	Mass spectrum of imine 2PC2ABA	53
1.20	Structure of 2PC2ABA	54
1.21	<sup>1</sup> Hnmr spectrum of imine 3PC3ABA	56
1.22	<sup>13</sup> Cnmr spectrum of imine 3PC3ABA	57
1.23	Mass spectrum of imine 3PC3ABA	58
1.24	Structure of 3PC3ABA	59
1.25	<sup>1</sup> Hnmr spectrum of imine 2PC2AP	60
1.26	<sup>13</sup> Cnmr spectrum of imine 2PC2AP	60
1.27	Mass spectrum of imine 2PC2AP	61
1.28	Structure of 2PC2AP	62
1.29	<sup>1</sup> Hnmr spectrum of imine 3FIPH	65
1.30	<sup>13</sup> Cnmr spectrum of imine 3FIPH	65
1.31	Mass spectrum of imine 3FIPH	66
1.32	Structure of 3FIPH	67
1.33	<sup>1</sup> Hnmr spectrum of imine 3FISC	69
1.34	<sup>13</sup> Cnmr spectrum of imine 3FISC	69
1.35	Mass spectrum of imine 3FISC	70
1.36	Structure of 3FISC and its keto-enol tautomerism	71
1.37	<sup>1</sup> Hnmr spectrum of imine 3FITSC	73
1.38	<sup>13</sup> Cnmr spectrum of imine 3FITSC	73
1.39	Mass spectrum of imine 3FITSC	74
1.40	Structure of 3FITSC and its thioketo-thioenol tautomerism	75

1.41	<sup>1</sup> Hnmr spectrum of imine 3FIDACH	77
1.42	<sup>13</sup> Cnmr spectrum of imine 3FIDACH	78
1.43	DEPT 135 spectrum of imine 3FIDACH	78
1.44	Mass spectrum of imine 3FIDACH	79
1.45	Structure of 3FIDACH	80
<b>PART II CORROSION INHIBITION STUDIES</b>		
2.1	Equivalent circuit model	134
2.2	Nyquist plot	136
2.3	Bode and impedance plots	137
2.4	Linear polarization plot	138
2.5	Tafel plot	141
2.6	Noise current Vs time plot	143
2.7	Pitting index curve	143
2.8	PSD plot	146
2.9	Variation of corrosion rate of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl.	149
2.10	Variation of inhibition efficiencies ( $\eta_w\%$ ) of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl	152
2.11	(a) Interaction of 2PCOX on carbon steel in 1.0M HCl, (b) Interaction of 3PCOX on carbon steel in 1.0M HCl	153
2.12	Comparison of corrosion inhibition efficiencies of heterocyclic imines of pyridine carbaldehyde and their parent amines on CS in 1.0M HCl.	155
2.13	El-Awady isotherm for 2PCOX on CS in 1.0M HCl	157
2.14	Langmuir isotherm for 3PCOX on CS in 1.0M HCl	157
2.15	El-Awady isotherm for 2PC4ABA on CS in 1.0M HCl	157
2.16	Temkin isotherm for 2PC3ABA on CS in 1.0M HCl	157
2.17	Langmuir isotherm for 2PC2ABA on CS in 1.0M HCl	157
2.18	Langmuir isotherm for 3PC3ABA on CS in 1.0M HCl	157
2.19	Langmuir isotherm for 2PC2AP on CS in 1.0M HCl	158
2.20	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 2PCOX in 1.0M HCl	160
2.21	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 3PCOX in 1.0M HCl	160
2.22	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 2PC4ABA in 1.0M HCl	161
2.23	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 2PC3ABA in 1.0M HCl	161
2.24	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 2PC2ABA in 1.0M HCl	161
2.25	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 3PC3ABA in 1.0M HCl	163

2.26	a) Arrhenius plots and b) log (K/T) Vs 1000/T plots for the corrosion of CS in the presence and absence of 2PC2AP in 1.0M HCl	163
2.27	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PCOX in 1.0M HCl	167
2.28	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3PCOX in 1.0M HCl	167
2.29	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC4ABA in 1.0 HCl	167
2.30	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC3ABA in 1.0M HCl	168
2.31	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC2ABA in 1.0M HCl	168
2.32	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3PC3ABA in 1.0M HCl	168
2.33	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC2AP in 1.0M HCl	169
2.34	Equivalent circuit fitted for EIS studies	170
2.35	Variation of corrosion inhibition efficiencies ( $\eta_{EIS}\%$ ) of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl	171
2.36	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PCOX in 1.0M HCl	172
2.37	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3PCOX in 1.0M HCl	173
2.38	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC4ABA in 1.0M HCl	173
2.39	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC3ABA in 1.0M HCl	173
2.40	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC2ABA in 1.0M HCl	174
2.41	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3PC3ABA in 1.0M HCl.	174
2.42	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC2AP in 1.0M HCl	174
2.43	Variation of corrosion inhibition efficiencies ( $\eta_{Rp}\%$ ) of heterocyclic imines of pyridine carbaldehyde on CS in 1.0M HCl	176
2.44	Noise current for CS in the presence and absence of heterocyclic imines of pyridine carbaldehyde (1.0mM) in 1.0M HCl	177
2.45	PSD curves of CS in a) blank b) 2PCOX c) 3PCOX d) 2PC4ABA e) 2PC3ABA f) 2PC2ABA g) 3PC3ABA h) 2PC2AP	178
2.46	Pitting index curves of CS in a) blank b) 2PCOX c) 3PCOX d) 2PC4ABA e) 2PC3ABA f) 2PC2ABA g) 3PC3ABA h) 2PC2AP	179
2.47	Optimized geometry of 2PCOX	182
2.48	Optimized geometry of 3PCOX	182



2.49	Optimized geometry of 2PC4ABA	182
2.50	Optimized geometry of 2PC3ABA	182
2.51	Optimized geometry of 2PC2ABA	183
2.52	Optimized geometry of 3PC3ABA	183
2.53	Optimized geometry of 2PC2AP	183
2.54	HOMO of 2PCOX	183
2.55	LUMO of 2PCOX	183
2.56	HOMO of 3PCOX	184
2.57	LUMO of 3PCOX	184
2.58	HOMO of 2PC4ABA	184
2.59	LUMO of 2PC4ABA	184
2.60	HOMO of 2PC3ABA	184
2.61	LUMO of 2PC3ABA	184
2.62	HOMO of 2PC2ABA	185
2.63	LUMO of 2PC2ABA	185
2.64	HOMO of 3PC3ABA	185
2.65	LUMO of 3PC3ABA	185
2.66	HOMO of 2PC2AP	185
2.67	LUMO of 2PC2AP	185
2.68	SEM images of a) bare metal b) metal immersed in 1.0M HCl c) metal immersed in 1.0M HCl containing 1.0mM 2PC2ABA	186
2.69	Variation of corrosion rate of heterocyclic imines of 3-formylindole carbaldehyde on CS in 1.0M HCl.	188
2.70	Variation of inhibition efficiencies ( $\eta_w\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on CS in 1.0M HCl	190
2.71	Comparison of corrosion inhibition efficiencies of heterocyclic imines of 3-formylindole carbaldehyde and their parent amines on CS in 1.0M HCl	191
2.72	Langmuir isotherm for 3FIPH on CS in 1.0M HCl	193
2.73	Langmuir isotherm for 3FISC on CS in 1.0M HC	193
2.74	Langmuir isotherm for 3FITSC on CS in 1.0M HCl	193
2.75	Langmuir isotherm for 3FIDACH on CS in 1.0M HCl	193
2.76	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FIPH in 1.0M HCl	195
2.77	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FISC in 1.0M HCl	196
2.78	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FITSC in 1.0M HCl	196
2.79	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FIDACH in 1.0M HCl	196
2.80	Variation of corrosion inhibition efficiencies ( $\eta_{EIS}\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on CS in 1.0M HCl	197
2.81	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FIPH in 1.0M HCl	199
2.82	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FISC in 1.0M HCl	199

2.83	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FITSC in 1.0M HCl	199
2.84	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FIDACH in 1.0M HCl	200
2.85	Variation of corrosion inhibition efficiencies ( $\eta_{Rp}\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on CS in 1.0M HCl	203
2.86	Noise current for CS in the presence and absence of heterocyclic imines of 3-formylindole carbaldehyde (1.0mM) in 1.0M HCl	204
2.87	PSD curves of CS in a) blank b) 3FIPH c) 3FISC d) 3FITSC e) 3FIDACH	204
2.88	Pitting index curves of CS in a) blank b) 3FIPH c) 3FISC d) 3FITSC e) 3FIDACH	205
2.89	Optimized geometry of 3FIPH	207
2.90	Optimized geometry of 3FISC	207
2.91	Optimized geometry of 3FITSC	208
2.92	Optimized geometry of 3FIDACH	208
2.93	HOMO of 3FIPH	208
2.94	LUMO of 3FIPH	208
2.95	HOMO of 3FISC	208
2.96	LUMO of 3FISC	208
2.97	HOMO of 3FITSC	209
2.98	LUMO of 3FITSC	209
2.99	HOMO of 3FIDACH	209
2.100	LUMO of 3FIDACH	209
2.101	SEM images of a) bare metal b) metal immersed in 1.0M HCl c) metal immersed in 1.0M HCl containing 1.0mM 3FITSC	210
2.102	Variation of corrosion rate of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	213
2.103	Variation of inhibition efficiencies ( $\eta_w\%$ ) of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	214
2.104	Temkin isotherm for 2PCOX on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	216
2.105	Langmuir isotherm for 3PCOX on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	216
2.106	El-Awady isotherm for 2PC4ABA on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	216
2.107	Langmuir isotherm for 2PC3ABA on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	216
2.108	Langmuir isotherm for 2PC2ABA on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	216
2.109	Langmuir isotherm for 3PC3ABA on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	216
2.110	Langmuir isotherm for 2PC2AP on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	217
2.111	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PCOX in 0.5M H <sub>2</sub> SO <sub>4</sub>	220
2.112	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3PCOX in 0.5M H <sub>2</sub> SO <sub>4</sub>	220
2.113	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC4ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	221
2.114	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC3ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	221

2.115	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC2ABA in 0.5M H <sub>2</sub> SO <sub>4</sub> .	221
2.116	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3PC3ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	222
2.117	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 2PC2AP in 0.5M H <sub>2</sub> SO <sub>4</sub> .	222
2.118	Variation of corrosion inhibition efficiencies ( $\eta_{EIS}\%$ ) of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	223
2.119	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PCOX in 0.5M H <sub>2</sub> SO <sub>4</sub>	224
2.120	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3PCOX in 0.5M H <sub>2</sub> SO <sub>4</sub>	224
2.121	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC4ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	224
2.122	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC3ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	226
2.123	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC2ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	226
2.124	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3PC3ABA in 0.5M H <sub>2</sub> SO <sub>4</sub>	226
2.125	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 2PC2AP in 0.5M H <sub>2</sub> SO <sub>4</sub>	227
2.126	a) Intramolecular H-bond in 2PCOX b) intermolecular H-bond in 3PCOX	227
2.127	Variation of corrosion inhibition efficiencies ( $\eta_{pol}\%$ ) of heterocyclic imines of pyridine carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	228
2.128	SEM images of a) bare metal b) metal immersed in 0.5M H <sub>2</sub> SO <sub>4</sub> c) metal immersed in 0.5M H <sub>2</sub> SO <sub>4</sub> containing 1.0mM 2PC2AP	229
2.129	Variation of corrosion rate of heterocyclic imines of 3-formylindole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	231
2.130	Variation of inhibition efficiencies ( $\eta_w\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	232
2.131	El-Awady isotherm for 3FIPH on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	234
2.132	Langmuir isotherm for 3FISC on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	234
2.133	Langmuir isotherm for 3FITSC on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	234
2.134	El-Awady isotherm for 3FIDACH on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	234
2.135	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FIPH in 0.5M H <sub>2</sub> SO <sub>4</sub>	237
2.136	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FISC in 0.5M H <sub>2</sub> SO <sub>4</sub>	238
2.137	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FITSC in 0.5M H <sub>2</sub> SO <sub>4</sub>	238
2.138	a) Nyquist plots and b) Bode plots of CS in the presence and absence of 3FIDACH in 0.5M H <sub>2</sub> SO <sub>4</sub>	238
2.139	Interaction of 3FIDACH on CS surface in 0.5M H <sub>2</sub> SO <sub>4</sub>	239

2.140	Variation of corrosion inhibition efficiencies ( $\eta_{EIS}\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	240
2.141	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FIPH in 0.5M H <sub>2</sub> SO <sub>4</sub>	243
2.142	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FISC in 0.5M H <sub>2</sub> SO <sub>4</sub>	243
2.143	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FITSC in 0.5M H <sub>2</sub> SO <sub>4</sub>	243
2.144	a) Tafel plots and b) Linear polarization plots of CS in the presence and absence of 3FIDACH in 0.5M H <sub>2</sub> SO <sub>4</sub>	244
2.145	Variation of corrosion inhibition efficiencies ( $\eta_{Rp}\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on CS in 0.5M H <sub>2</sub> SO <sub>4</sub>	244
2.146	SEM images of a) bare metal b) metal immersed in 0.5M H <sub>2</sub> SO <sub>4</sub> c) metal immersed in 0.5M H <sub>2</sub> SO <sub>4</sub> containing 1.0mM 3FITSC	245
2.147	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 2PCOX in 0.1M HNO <sub>3</sub>	251
2.148	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 3PCOX in 0.1M HNO <sub>3</sub>	251
2.149	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 2PC4ABA in 0.1M HNO <sub>3</sub>	251
2.150	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 2PC3ABA in 0.1M HNO <sub>3</sub>	253
2.151	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 2PC2ABA in 0.1M HNO <sub>3</sub>	253
2.152	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 3PC3ABA in 0.1M HNO <sub>3</sub>	253
2.153	a) Nyquist plots and b) Bode plots of Cu in the presence and absence of 2PC2AP in 0.1M HNO <sub>3</sub>	254
2.154	H-bond present in a) 2PCOX and b) 3PCOX	255
2.155	Variation of corrosion inhibition efficiencies ( $\eta_{EIS}\%$ ) of heterocyclic imines of pyridine carbaldehyde on Cu in 0.1M HNO <sub>3</sub>	256
2.156	Langmuir isotherm for 3PCOX on Cu in 0.1M HNO <sub>3</sub>	258
2.157	Langmuir isotherm for 2PC4ABA on Cu in 0.1M HNO <sub>3</sub>	258
2.158	EI-Awady isotherm for 2PC3ABA on Cu in 0.1M HNO <sub>3</sub>	258
2.159	Langmuir isotherm for 2PC2ABA on Cu in 0.1M HNO <sub>3</sub>	258
2.160	Freundlich isotherm for 3PC3ABA on Cu in 0.1M HNO <sub>3</sub>	258
2.161	Langmuir isotherm for 2PC2AP on Cu in 0.1M HNO <sub>3</sub>	258
2.162	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 2PCOX in 0.1M HNO <sub>3</sub>	261
2.163	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 3PCOX in 0.1M HNO <sub>3</sub>	261
2.164	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 2PC4ABA in 0.1M HNO <sub>3</sub>	262
2.165	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 2PC3ABA in 0.1M HNO <sub>3</sub>	262

2.166	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 2PC2ABA in 0.1M HNO <sub>3</sub>	262
2.167	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 3PC3ABA in 0.1M HNO <sub>3</sub>	264
2.168	Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 2PC2AP in 0.1M HNO <sub>3</sub>	264
2.169	Variation of corrosion inhibition efficiencies ( $\eta_{pol}\%$ ) of heterocyclic imines of pyridine carbaldehyde on copper in 0.1M HNO <sub>3</sub>	265
2.170	SEM images of a) bare metal b) Cu immersed in 0.1M HNO <sub>3</sub> c) Cu immersed in 0.1M HNO <sub>3</sub> containing 1.0mM 3PCOX d) Cu immersed in 0.1M HNO <sub>3</sub> containing 1.0mM 2PCOX	268
2.171	a) Nyquist plots and b) Bode plots of copper in the presence and absence of 3FIPH in 0.1M HNO <sub>3</sub>	270
2.172	a) Nyquist plots and b) Bode plots of copper in the presence and absence of 3FISC in 0.1M HNO <sub>3</sub>	270
2.173	a) Nyquist plots and b) Bode plots of copper in the presence and absence of 3FITSC in 0.1M HNO <sub>3</sub>	271
2.174	a) Nyquist plots b) Bode plots of copper in the presence and absence of 3FIDACH in 0.1M HNO <sub>3</sub>	271
2.175	Variation of corrosion inhibition efficiencies ( $\eta_{EIS}\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on Cu in 1.0M HNO <sub>3</sub>	273
2.176	Langmuir isotherm for 3FIPH on Cu in 0.1MHNO <sub>3</sub>	274
2.177	Langmuir isotherm for 3FISC on Cu in 0.1MHNO <sub>3</sub>	274
2.178	Langmuir isotherm for 3FITSC on Cu in 0.1MHNO <sub>3</sub>	275
2.179	Langmuir isotherm for 3FIDACH on Cu in 0.1MHNO <sub>3</sub>	275
2.180	a) Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 3FIPH in 0.1M HNO <sub>3</sub>	276
2.181	a) Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 3FISC in 0.1M HNO <sub>3</sub>	276
2.182	a) Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 3FITSC in 0.1M HNO <sub>3</sub>	277
2.183	a) Tafel plots and b) Linear polarization plots of Cu in the presence and absence of 3FIDACH in 0.1M HNO <sub>3</sub>	277
2.184	Interaction of 3FITSC on Cu surface	278
2.185	Variation of corrosion inhibition efficiencies ( $\eta_{pol}\%$ ) of heterocyclic imines of 3-formylindole carbaldehyde on Cu in 1.0M HNO <sub>3</sub>	279
2.186	SEM images of a) bare metal b) Cu immersed in 0.1M HNO <sub>3</sub> c) Cu immersed in 0.1M HNO <sub>3</sub> containing 1.0mM 3FITSC	280
<b>PART III CORROSION INHIBITION BY PROTECTIVE COATINGS</b>		
3.1	Electrode assembly in cyclic voltammetric technique	308
3.2	Cyclic voltammograms of a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP	313

3.3	Schematic diagrams for the conversion of various forms of PANI	314
3.4	Nyquist plots of CS specimens coated with various polyamino compounds kept for 24h in air and treated in 1.0M HCl a) blank b) PANI c) P2ABA d) P3ABA e) P2ABSA f) P2NA g) P3NA h) P2AP	317
3.5	Nyquist plots of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h a) blank b) PANI c) P2ABA d) P3ABA e) P2ABSA f) P2NA g) P3NA h) P2AP	318
3.6	Intermolecular hydrogen bond in P2ABA	321
3.7	Equivalent circuit suitable for the uncoated metal specimens (Randles circuit)	324
3.8	Equivalent circuit suitable for the coated metal specimens (Warburg impedance circuit)	324
3.9	Double layer capacitance Vs corrosion protection efficiency of polymeric coated CS specimens in 1.0M HCl at condition 1	325
3.10	Tafel plots of CS specimens coated with polyamino compounds kept for 24h in air and treated in 1.0M HCl a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP	327
3.11	Tafel plots of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP	328
3.12	FTIR spectra of chemically synthesized and electrochemically coated polyamino compounds a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP	332
3.13	SEM images of a) bare metal b) uncoated steel specimen immersed in 1.0M HCl for 24h c) P2ABSA coated steel specimen kept for 24h in air and immersed in 1.0M HCl d) P2ABSA coated steel specimen directly immersed in 1.0M HCl (100ml) for 24h	335