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}Hnmr, ^{13}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}Hnmr, ^{13}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^{0}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_2SO_4 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_2SO_4 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_2SO_4 is included in section II. The description on anticorrosive properties of heterocyclic imines on copper in 0.1M HNO_3 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_3. 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_3. 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_2SO_4 media and also on copper in HNO_3 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^{0}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_3 media. Relatively poor inhibition efficacy was exhibited by these imines in H_2SO_4 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

LIST OF TABLES

LIST OF FIGURES