

**ELECTROCHEMICAL STUDIES ON N, S, O DONOR  
HETEROCYCLES AS CORROSION PROTECTION  
AGENTS FOR COMMERCIAL METALS IN  
DIFFERENT ENVIRONMENTS**

*Thesis*  
*Submitted to the University of Calicut*  
*For the award of the degree of*

**DOCTOR OF PHILOSOPHY IN CHEMISTRY**

**REVATHI MOHAN**



**DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALICUT  
KERALA-673635  
INDIA  
SEPTEMBER-2015**

## **CERTIFICATE**

This is to certify that the thesis entitled “**Electrochemical studies on N, S, O donor heterocycles as corrosion protection agents for commercial metals in different environments**” submitted by **Revathi Mohan** to University of Calicut for the award of the degree of Doctor of Philosophy in Chemistry, is the result of bona fide research work carried out in the Department of Chemistry, University of Calicut under my guidance and supervision. The contents in the thesis have been checked for plagiarism using the software ‘Urkund’ and similarity index falls under permissible limit. I further certify that the thesis or part therefore has not previously formed the basis for the award of any degree, diploma or associate ship of any other university or institute.

University of Calicut

**Dr. Abraham Joseph**

September- 2015

## **DECLARATION**

I hereby declare that the matter embodied in the thesis is the result of studies carried out by me in the Department of Chemistry, University of Calicut, under the supervision of **Dr. Abraham Joseph**, Associate professor, Department of Chemistry, University of Calicut and the same has not previously formed the basis for the award of any degree or diploma. Whenever the work described or cited is based on the findings of other researchers, due acknowledgement is made in keeping with the general practice of reporting scientific observations.

**Revathi Mohan**

## **ACKNOWLEDGEMENT**

*First of all, I would like to thank my guide, **Dr. Abraham Joseph** for his constant support and guidance throughout my research work, without it, the completion of this work would have been impossible. He had been a guiding force in the proper execution of my work. .*

*I would like to express my sincere thanks to the Head of the Department, Dr. K. Muraleedharan and former Heads of the Department, Dr. V.M. Abdul Mujeeb and Dr. Ganga Devi for providing me all the facilities to carry out my research work.*

*Words cannot express my gratitude towards Mr. Noushad Thayyil for sharing his valuable knowledge in Computational Chemistry with me. I'm also extending my thanks to my seniors, Dr. Sam John and Dr. Bincy Joseph.*

*There are two people who require special mention, Ms. Anupama K.K. and Mrs. Ramya Bhagyaraj. I can never forget the selfless help rendered by them, in completing my work.*

*I would also like to thank Ms. Anupama R. Prasad, Ms. Shainy K.M and Mr. Mathew Kuruvilla and all others in my research group for their help and support.*

*I also thank all other research scholars in the Department of Chemistry for their unconditional support and assistance.*

*I also thank Mr. Satheesan K, technical assistant and other members of the non-teaching staff in the Department of Chemistry, University of Calicut.*

*I am using this opportunity to acknowledge, the financial support received from UGC, New Delhi for providing me with JRF and SRF throughout my research period, with gratitude.*

*I can never forget the love, support, care and encouragement provided by my family.*

*Last but not the least; I thank God Almighty whose invisible support helped me to submit my thesis.*

To

*My family for the unconditional support and care*

# CONTENTS

<b>Chapter</b>	<b>Title</b>	<b>Page No.</b>
<b>I</b>	INTRODUCTION	1-38
<b>II</b>	MATERIALS AND METHODS	39-59
<b>III</b>	CORROSION INHIBITION OF COPPER IN NITRIC ACID USING ALKYL BENZIMIDAZOLES	60-86
<b>IV</b>	INHIBITION OF COPPER CORROSION IN ACID MEDIA USING EMBA AND EEBA	87-110
<b>V</b>	INHIBITION OF MILD STEEL CORROSION IN HYDROCHLORIC ACID USING EMBA	111-135
<b>VI</b>	CORROSION INHIBITION OF MILD STEEL IN 1 N HYDROCHLORIC ACID USING SYNERGISTIC INTERACTION OF EMBA WITH TSC AND BTZ	136-154
<b>VII</b>	INHIBITION OF MILD STEEL CORROSION IN HYDROCHLORIC ACID USING EBI AND EEBA	155-185
<b>VIII</b>	CORROSION INHIBITION OF MILD STEEL IN HYDROCHLORIC ACID USING EPBA	186-197
<b>IX</b>	INHIBITION OF MILD STEEL CORROSION IN HYDROCHLORIC ACID USING PBI	198-216
	REFERENCES	217-220
	APPENDIX	
	LIST OF PRESENTATIONS	
	LIST OF PUBLICATIONS	
	COPY OF PUBLICATION	

# Preface

Revathi Mohan “Electrochemical studies on N,S,O Donor heterocycles as corrosion protection agents for commercial metals in different Environments” Thesis. Department of Chemistry, University of Calicut, 2015

**General**

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. In fact, electrochemistry encompasses a huge array of different phenomena (e.g., electrophoresis and corrosion), devices (electrochromic displays, electro analytical sensors, batteries and fuel cells), and technologies (the electroplating of metals and the large-scale production of aluminium and chlorine). Corrosion is defined as destruction or deterioration of a material because of reaction with its environment. Corrosion can be fast or slow. The present work focuses on studying the corrosion inhibition properties of alkyl benzimidazoles and their derivatives on commercial metals such as mild steel and copper in acids such as nitric acid and hydrochloric acid.

**CHAPTER I: INTRODUCTION**

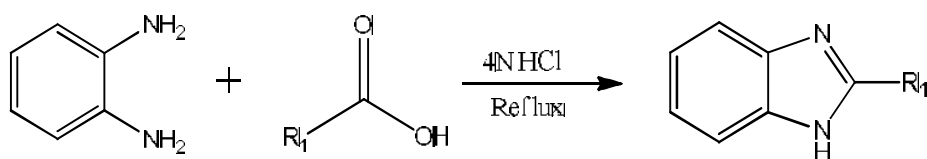
This chapter deals with some of the basic aspects of corrosion. It also explains how corrosion affects the economy and need for taking proper measures to reduce corrosion. Different classification of corrosion has been mentioned in this chapter. Corrosion has been classified into uniform and non-uniform or localized corrosion. And again localized corrosion has been classified into pitting, crevice corrosion, intergranular corrosion, de-alloying, hydrogen damage, etc. Fundamentals of corrosion electrochemistry have also been discussed

in this chapter. The different types of charge transfer reactions taking place in an electrode interface have been mentioned under this section. The basic electrochemical reactions that lead to corrosion have been briefly outlined in this chapter. The concept of polarization is briefly discussed here because of its importance in understanding corrosion behaviour and corrosion reactions. The role of electrolytes in promoting corrosion was explained. Electrode potential and structure of the electrode interface has been discussed. A brief description of the basic thermodynamics of corrosion has been furnished in this chapter. Another important aspect of corrosion discussed in this chapter is corrosion inhibitor. The different types of inhibitors available, methods to calculate inhibition efficiency, influence of inhibitor concentration, solution pH and hydrodynamic conditions on inhibition efficiency, inhibition by adsorption and mechanism of corrosion in the presence of adsorbed layers were explained. A detailed description of various quantum chemical methods available for calculating molecular geometries, reactivity and other properties of inhibitor molecules, nature of adsorption, way of interaction etc. has been furnished.

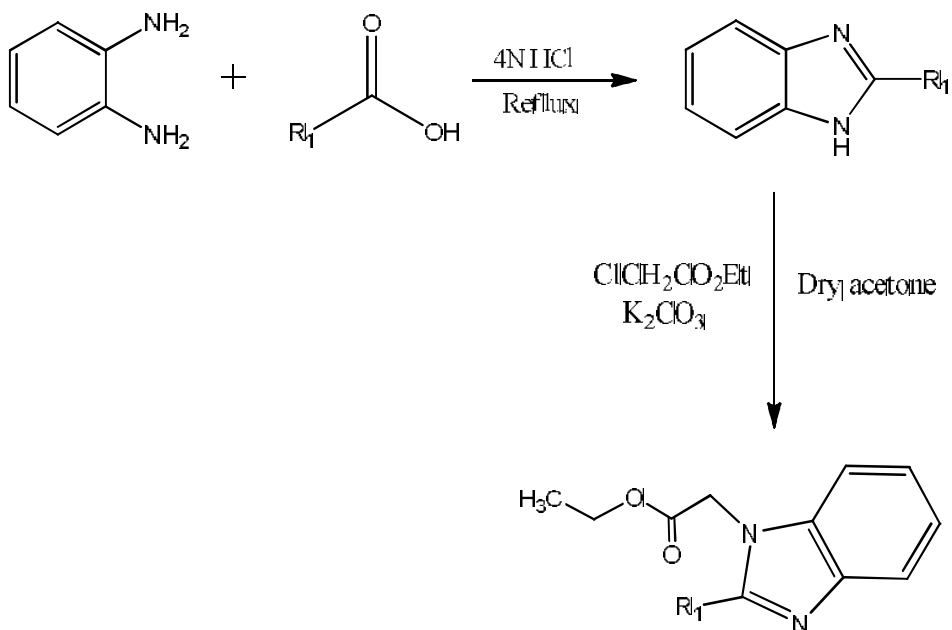
## **CHAPTER II: MATERIALS AND METHODS**

The different types of metals used for study and the sample preparation, inhibitors used and their synthesis, etc were explained in detail under this section. The metals used were copper and mild steel. The different types of inhibitors used were 2-methylbenzimidazole, 2-ethylbenzimidazole, 2-propylbenzimidazole, ethyl(2-methylbenzimidazolyl)acetate, ethyl(2-ethylbenzimidazolyl)acetate and ethyl(2-propylbenzimidazolyl)acetate. A mixture of o-phenylenediamine (10 g, 0.092 moles) and aliphatic acid (0.11 moles) was dissolved in 4 M HCl

(10 ml) and refluxed at 100<sup>0</sup>C for 12 hours. Completion of the reaction was monitored by TLC. The contents were cooled to room temperature and neutralized with saturated solution of NaHCO<sub>3</sub>. The aliphatic acid used for the preparation of 2-methylbenzimidazole was acetic acid. Propionic acid was used for the preparation of 2-ethylbenzimidazole and butyric acid was used for the preparation of 2-propylbenzimidazole.



For the synthesis of ethyl(2-alkylbenzimidazolyl)acetate. The solution of 2-alkylbenzimidazole (0.062 mole) in acetone (20 mL) was mixed with ethylchloroacetate (7.9 mL, 0.074 mole) and potassium carbonate (16.5 g, 0.12 mole) and refluxed for 6 hr. Completion of the reaction was monitored by TLC. The reaction mixture was filtered. From the clear filtrate, excess acetone was removed by distillation and then was added to water. The solid product separated was collected by filtration and dried. Further purification was done by crystallization from ethyl acetate to give ethyl(2-alkylbenzimidazolyl)acetate.

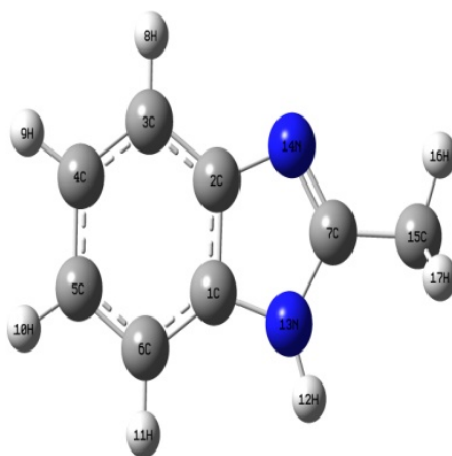


The various methods used for studying corrosion were explained in detail in this chapter. This chapter gives a basic idea about corrosion testing using electrochemical polarization techniques and the various components involved in it. The electrochemical studies are carried out using a three electrode cell assembly. In the three electrode system, working electrode is the metal sample, auxiliary electrode is platinum electrode (1 cm<sup>2</sup> surface area) and reference electrode is calomel electrode. The studies were carried out using Gill AC computer controlled electrochemical work station [ACM, UK (model no: 1475)]. A brief description about techniques such as electrochemical impedance spectroscopy, potentiodynamic

polarization study, adsorption study, computational study, scanning electron microscopy, atomic force microscopy, etc. were given.

### **CHAPTER III: CORROSION INHIBITION OF COPPER IN NITRIC ACID USING ALKYL BENZIMIDAZOLES**

The interaction and corrosion inhibition properties of alkyl benzimidazoles (2-methylbenzimidazole, 2-ethylbenzimidazole and 2-propylbenzimidazole) on copper in 1 N HNO<sub>3</sub> at different temperatures (303, 308 and 313 K) have been studied using EIS, polarization, adsorption studies and computational calculations. The molecules acted as effective inhibitors for copper corrosion. Polarization studies showed that the molecules behave as mixed type inhibitors. The inhibition efficiency of both the inhibitors was found to decrease with increase in temperature. The mechanism involves adsorption of inhibitor molecules on the metal surface.

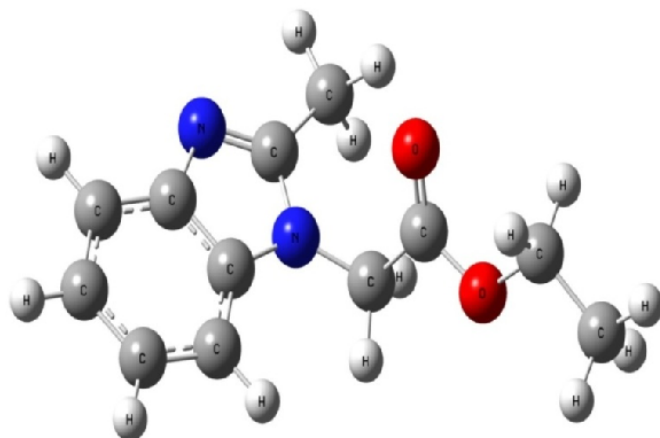


Optimized geometry for 2-methylbenzimidazole

#### **CHAPTER IV: INHIBITION OF COPPER CORROSION IN ACID MEDIA USING EMBA AND EEBA**

Electrochemical measurements such as EIS and potentiodynamic polarization were used to study the corrosion inhibition efficiency of EMBA in various concentrations of HCl ranging from 0.5 to 1.5 N and also in different concentrations of HNO<sub>3</sub> ranging from 0.5 to 1.5 N. The corrosion inhibition efficiency of EEBA in different concentrations of HCl ranging from 0.5 to 1.5 N was also studied. The inhibition efficiency of EMBA and EEBA increases with increase in its concentration at room temperature. EMBA is more efficient for 0.5 NHNO<sub>3</sub> and for HCl, EMBA is more efficient in 1.5 N. EEBA had maximum efficiency in 0.5 N HCl. In 0.5 and 1 N HCl, EEBA showed more efficiency and in 1.5 N HCl, EMBA had more corrosion inhibition efficiency than EEBA. The mode of inhibition of both the inhibitors was through adsorption on to the copper surface. The mode of adsorption was believed to be both physisorption and chemisorption.

The adsorption obeyed Langmuir adsorption isotherm. Various quantum chemical parameters as well as optimized geometry of the inhibitors were calculated. The Fukui indices were also calculated.

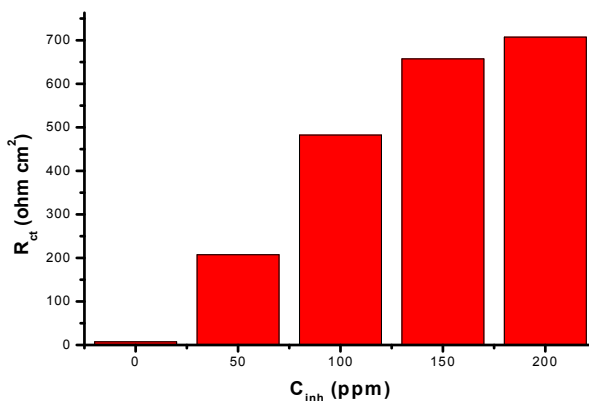


Optimized geometry of EMBA

## **CHAPTER V: INHIBITION OF MILD STEEL CORROSION IN HYDROCHLORIC ACID USING EMBA**

The corrosion inhibition properties of ethyl(2-methylbenzimidazolyl)acetate (EMBA) and its derivative on mild steel in hydrochloric acid (0.5, 5 and 1.5 N) at different temperatures (303, 308 and 313 K) have been studied using EIS, polarization adsorption studies and computational calculations. EMBA acted as effective inhibitor for mild steel corrosion. The inhibition efficiency of EMBA increases with increase in its concentration at room temperature. The efficiency was found to decrease with increase in its concentration. The inhibition efficiency of EMBA was found to decrease with increase in concentration of HCl solution. Polarization studies showed that EMBA act as a mixed type inhibitor. The mode of inhibition of EMBA was through adsorption on to the mild steel surface. The mode

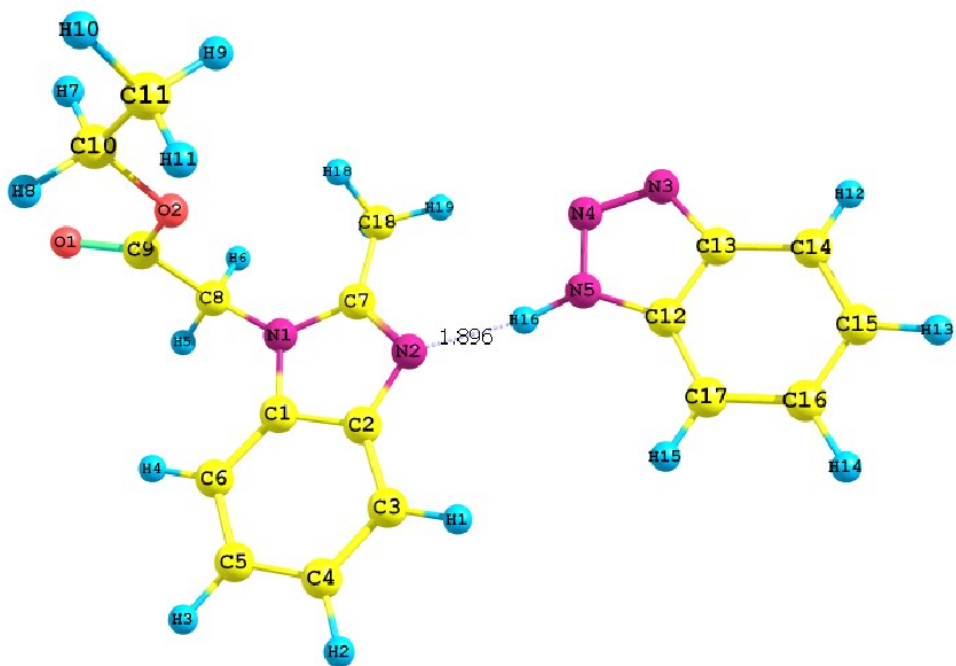
of adsorption was believed to be both physisorption and chemisorption. The adsorption obeyed Langmuir adsorption isotherm.



Plot of charge transfer resistance ( $R_{ct}$ ) with respect to EMBA concentrations( $C_{inh}$ )

## **CHAPTER VI: CORROSION INHIBITION OF MILD STEEL IN 1 N HCl USING SYNERGISTIC INTERACTION OF EMBA WITH TSC AND BTZ**

Synergistic interaction of EMBA-TSC and EMBA-BTZ pairs and their corrosion inhibition properties on mild steel in 1 N HCl at different temperatures have been studied using EIS, potentiodynamic polarization, adsorption and computational studies. Both the pairs acted as effective inhibitors for mild steel in HCl. The adsorption of the inhibitors followed Langmuir adsorption isotherm

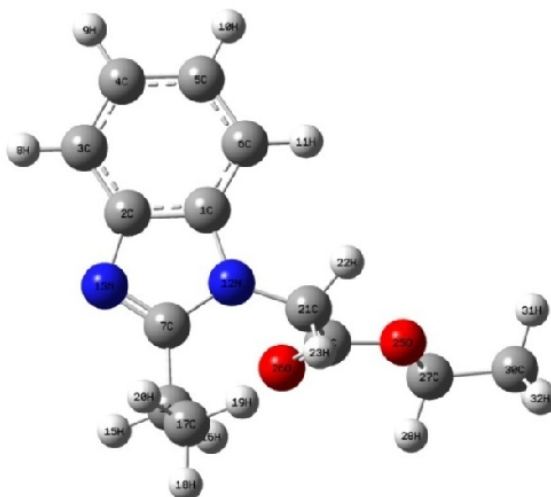


Optimized geometry for the interaction of EMBA-BTZ pair

## CHAPTER VII:INHIBITION OF MILD STEEL CORROSION IN HYDROCHLORIC ACID USING EBI AND EEBA

The interaction and corrosion inhibition properties of 2-ethylbenzimidazole and its derivative ethyl(2-ethylbenzimidazolyl)acetate (EEBA) on mild steel in hydrochloric acid (0.5, 5 and 1.5 M) at different temperatures (303, 308 and 313 K) have been studied using EIS, polarization and adsorption studies and computational calculations. Both EBI and EEBA acted as effective inhibitors of mild steel corrosion. Polarization studies showed that both molecules act as mixed type inhibitors. EEBA was having more inhibition efficiency than EBI. The inhibition efficiency of both the inhibitors was found to decrease with increase in temperature. The

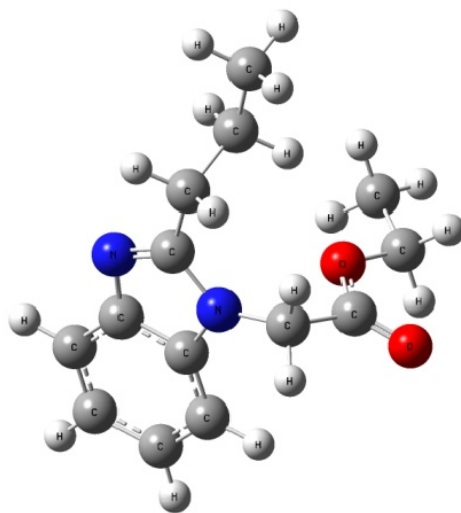
mechanism involves adsorption of inhibitor molecules on the metal surface.



Optimized geometry for EEBA

## **CHAPTER VIII: CORROSION INHIBITION OF MILD STEEL IN HYDROCHLORIC ACID USING EPBA**

The interaction and corrosion inhibition properties of ethyl(2-proylbenzimidazolyl)acetate (EPBA) on mild steel in hydrochloric acid (0.5, 1 and 1.5 N) at different temperatures (303, 308 and 313 K) have been studied using EIS, polarization and adsorption studies and computational calculations. EPBA acted as effective inhibitors of mild steel corrosion. Polarization studies showed that the molecule acted as mixed type inhibitor. The inhibition efficiency was found to decrease with increase in temperature. The mechanism involves adsorption of inhibitor molecules on the metal surface. Adsorption obeyed Langmuir adsorption isotherm.

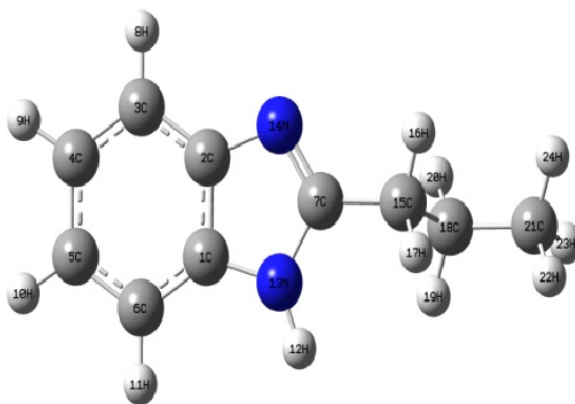


Optimized geometry for EPBA

## **CHAPTER IX: INHIBITION OF MILD STEEL CORROSION IN HCl USING PBI**

Electrochemical measurements such as EIS and potentiodynamic polarization techniques were used to study the corrosion inhibition efficiency of PBI in various concentrations of HCl ranging from 0.5 to 1.5 N at temperatures 303, 308 and 313 K. PBI acted as efficient inhibitor for the corrosion of mild steel in HCl. The inhibition efficiency of PBI increases with increase in its concentration at all the three temperatures studied. The inhibition efficiency of PBI was found to decrease with increase in concentration of HCl solution. The mode of inhibition of PBI was through adsorption on to the mild steel surface. The mode of adsorption was believed to be both physisorption and chemisorption. The adsorption obeyed Langmuir adsorption

isotherm in all the cases except for that in 1.5 N HCl at 313 K which obeyed Temkin adsorption isotherm.



Optimized geometry for 2-propylbenzimidazole