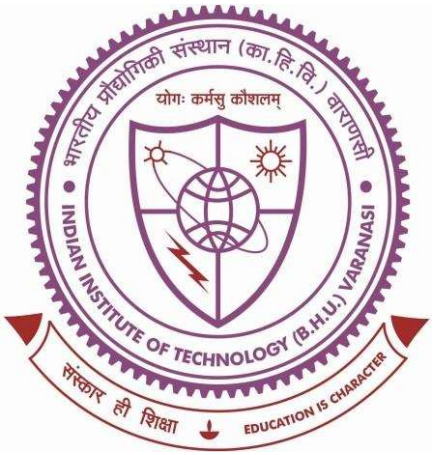
Heterocyclic compounds as acidizing corrosion inhibitors for carbon steel in acid media



Thesis submitted in partial fulfillment for the Award of Degree

Doctor of Philosophy

By

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It is further certified that the student has fulfilled all tha requirement of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.

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I, ***"Mohammad Salman"*** certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***"Prof.Vandana Srivastava"*** from ***"December 2017"*** to ***"2022"*** at the ***"Departement of Chemistry,"*** **Indian Institute od Technology, Banaras Hindu University,varanasi.** The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfullyt acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any others work, Paragraphs, text, data, results, etc., reported in journals, books, magazines, reports, dissertations, thesis etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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(Mohammad Salman)

(Research Scholar)

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Abbreviations used

$IE\%$=Percentage of inhibition efficiency

C_R=Corrosion rate ($mgcm^{-2}h^{-1}$)

C_R^o=Corrosion rate in uninhibited system ($mgcm^{-2}h^{-1}$)

C_R^i= Corrosion rate in inhibited system ($mgcm^{-2}h^{-1}$)

Y^0 =amplitude of the CPE ($s^n\Omega^{-1}cm^{-2}$)

j= imaginary unit ($\sqrt{-1}$)

ω=angular frequency ($2\pi f$, f the frequency)

f = Frequency of component of impedance (s^{-1})

C_{dl}=Double layer capacitance ($\mu F\ cm^{-2}$)

C_f=film capacitance

C=capacitance

R_s=Solution resistance(Ωcm^2)

R_L=Inductance resistance (Ωcm^2)

R_{ct}=charge transfer resistance in absence of inhibitor(Ωcm^2)

R_p=polarization resistance ($\Omega\ cm^2$)

i^0_{corr}=Corrosion current density in uninhibited solution

(μAcm^{-2})i^i_{corr}= Corrosion current density in inhibited solution (μA

cm^{-2})E_{corr}=Corrosion potential (mV/SCE)

β_a=Anodic Tafel constant ($mV\ dec^{-1}$)

β_c=Cathodic Tafel constant ($mV\ dec^{-1}$)

A=Arrhenius pre-exponential factor ($mgcm^{-2}\ h^{-1}$)

E_a=Activation energy(kJmol^{-1})

R=Universal gas constant (JK^{-1}mol^{-1})

T=Absolute temperature (K)

N =Avogadro's number (6.023×10^{23}mol^{-1})

h=Planck's constant (J-s)

K_{ads}=Adsorption equilibrium constant (Lmol^{-1})

$\Delta G°_{ads}$=Gibbs freeenergy of adsorption(kJmol^{-1})

θ=Degree of surface coverage of metal

C_{inh}=Concentration of inhibitor (molL^{-1},ppm)

E_{HOMO}=Energy of highest occupied molecular orbital

E_{LUMO}=Energy of lowest unoccupied molecular orbital

ΔE=Energygap between HOMO and LUMO

χ_{Fe}=Electro negativity of iron

χ_{inh}=Electronegativity of inhibitor

σ= softness

η_{Fe} =Hardness of iron

η_{inh}=Hardness of inhibitor

Φ=work function

ΔN=Fraction of electron transfer

$E_{molecule}$=Energy of the inhibitor molecule before adsorption of inhibitor molecules

$E_{interaction}$= Interaction energy between metal surface and inhibitor molecules

PREFACE

Corrosion is a gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment. Corrosion causes numerous failures and enormous loses in a number of industries. Failures resulting from inability of metal to support the designed load requirement due to loss of metal caused by corrosion effect can be controlled economically using the chemical inhibitors. Besides the effectiveness, most of the chemical inhibitors are associated with toxicity, disposal and enormous cost. The present research work has been focused on Synthesis of Heterocyclic compounds as acidizing corrosion inhibitors for carbon steel in 15% hydrochloric acid. The thesis is divided into five chapters.

Chapter 1 deals with the introduction of corrosion, highlighting the definition of corrosion, Economic importance of corrosion, Different form of corrosion, Methods of Corrosion Control, theory and mechanism of corrosion principles. Aim and objectives of the research have been elaborated.

Chapter 2 focuses on the literature survey relevant to corrosion of carbon steel (N-80 Steel and mild steel) in the acid environment, along with the general introduction of corrosion inhibitors: definition, types and mechanism. Chapter 3 deals with the materials and methods details including materials, synthesis of organic inhibitors, sample preparation, chemicals and methods adopted such weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), surface analysis (SEM/EDX/AFM /FTIR) and computational simulations.

(quantum chemical calculations and molecular dynamic) for the evaluation of corrosion inhibition property have been described.

Chapter 4 deals with the results and discussion on corrosion inhibition of N-80 steel and mild steel in 15% hydrochloric acid by four series of inhibitors: Substituted Triazines (TZs) derivatives (Series I), Chromeno Naphthyridines (CNs) derivatives (Series II), Quinolines (AHQs) (Series III) and Benzimidazole based corrosion inhibitors (Series IV) using weight loss (WL), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP). The inhibited and uninhibited metal surface was characterized using the scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), Fourier-transform infrared Spectroscopy-Attenuated total reflection- (FTIR-ATR) and UV–vis spectroscopy. The theoretical studies: quantum chemical calculation and molecular dynamics simulation were used to obtain insights in the inhibition mechanism of the inhibitor molecules on the metal surface.

A plausible mechanism of corrosion inhibition has been proposed on the basis of experimentally and theoretically obtained results.

Chapter 5 provides general summary, conclusions and suggests future work.