
TABLE OF CONTENTS

	Page
Chapter 1: Introduction	1-40
1. Introduction	1
1.1 Basic concepts of corrosion	2
1.2 Theories of corrosion	4
1.2.1 Chemical or Dry corrosion	4
1.2.2 Electrochemical or Wet corrosion	5
1.3 Types of corrosion	6
1.4 Factors influencing corrosion	8
1.4.1 Nature of the metal	8
1.4.2 Nature of environment	9
1.5 Thermodynamic aspects of corrosion	9
1.6 Pourbaix Diagram	11
1.7 Kinetic aspects of corrosion	12
1.7.1 Kinetic approach for equilibrium at an electrode	13
1.7.2 Electrochemical polarization	15
1.7.2.1 Activation polarization	15
1.7.2.2 Concentration polarization	17
1.7.2.3 Ohmic Resistance	20
1.8 Mixed Potential theory and Evans Diagram	20
1.9 Tafel extrapolation method	22
1.10 Electrochemical impedance spectroscopy	24
1.11 Corrosion control methods	26
1.12 Corrosion inhibitors	27
1.12.1 Classification of corrosion inhibitors	27
1.12.2 Environmental conditioners	27
1.12.3 Interface inhibitors	27

1.12.3 (a) Anodic inhibitors	27
1.12.3 (b) Cathodic inhibitors	28
1.12.3 (c) Mixed inhibitors	29
1.12.4 Interface inhibitors (Vapour phase)	30
1.13 Adsorption of inhibitors	30
1.13.1 Electrostatic adsorption	30
1.13.2 Physisorption	30
1.13.3 Chemisorption	31
1.14 Adsorption isotherms	31
1.15 Corrosion inhibition of mild steel in mineral acids	32
1.16 Application of theoretical methods in corrosion inhibitor studies	33
1.17 Literature survey on organic compounds as corrosion inhibitors	34
1.18 Objectives of the present work	40
Chapter 2: Experimental	41-56
2. Materials and methods	41
2.1 Materials	41
2.1.1 Composition and dimensions of used mild steel sample	41
2.1.2 Test solution	41
2.1.3 Inhibitors	41
2.2 Synthesis of inhibitors	42
2.3 Equipments and techniques used	48
2.3.1 Weight loss method for determination of corrosion rate	48
2.3.2 Electrochemical measurements	50
2.3.2.1 Electrochemical impedance spectroscopy	50
2.3.2.2 Potentiodynamic polarization	51
2.4 Thermodynamic parameters	52
2.4.1 Activation energy	52
2.4.2 Free energy of adsorption	52
2.5 Scanning electron microscopy	53
2.6 Atomic force microscopy	53

2.7 X-ray photoelectron spectroscopy	53
2.8 Quantum chemical calculations	54
2.9 Monte Carlo simulation	56
Chapter 3: Results and Discussion	57-126
3. Evaluation of corrosion inhibitors for mild steel in 1 M hydrochloric acid	57
3.1 Nicotinonitriles as corrosion inhibitor	57
3.1.1 Weight loss measurements	58
3.1.1.1 Effect of inhibitor concentrations	58
3.1.1.2 Effect of Temperature	60
3.1.1.3 Adsorption isotherm	60
3.1.2 Electrochemical measurements	62
3.1.2.1 Electrochemical impedance spectroscopy	62
3.1.2.2 Potentiodynamic polarization measurements	64
3.1.3 Surface characterization	66
3.1.4 Quantum chemical calculations	68
3.1.5 Monte Carlo simulation	72
3.2. Naphthyridines as corrosion inhibitors	76
3.2.1 Weight loss measurements	77
3.2.1.1 Effect of inhibitor concentrations	77
3.2.1.2 Effect of Temperature	78
3.2.1.3 Adsorption isotherm	79
3.2.2 Electrochemical measurements	80
3.2.2.1 Electrochemical impedance spectroscopy	80
3.2.2.2 Potentiodynamic polarization measurements	82
3.2.3 Surface characterization	84
3.2.4 Quantum chemical calculations	85
3.2.5 Monte Carlo simulation	90
3.3 Quinolines as corrosion inhibitors	93
3.3.1 Weight loss measurements	94
3.3.1.1 Effect of inhibitor concentration	94

3.3.1.2 Effect of Temperature	95
3.3.1.3 Adsorption isotherm	97
3.3.2 Electrochemical measurements	98
3.3.2.1 Electrochemical impedance spectroscopy	98
3.3.2.2 Potentiodynamic polarization measurements	101
3.3.3 Surface characterization	103
3.4 Thiopyrimidines as corrosion inhibitors	108
3.4.1 Weight loss measurement	109
3.4.1.1 Effect of inhibitor concentration	109
3.4.1.2 Effect of temperature	110
3.4.1.3 Adsorption isotherm	112
3.4.2 Electrochemical measurements	114
3.4.2.1 Electrochemical impedance spectroscopy	114
3.4.2.2 Potentiodynamic polarization measurements	117
3.4.3 Surface characterization	118
Chapter 4: Summary and Future work	127-133
References	134-147
List of Publications and Conferences	148-150

LIST OF FIGURES

Figure 1.1 Pictorial representation of corrosion cycle	2
Figure 1.2 Schematic representation of electrochemical corrosion cell where potential difference between the two sites drives the corrosion current	3
Figure 1.3 Pourbaix diagram for the iron/water system	12
Figure 1.4 Schematic energy profiles for equilibrium at an electrode. ΔG^* is Gibb's free energy of activation	14
Figure 1.5 Schematic energy profile for activation polarization at an electrode: ΔG^* = Gibb's free energy of activation; η/V anodic overpotential	16
Figure 1.6 Plot between logarithmic current density i , with overvoltage η (after polarization). In the plot the deviation from tafel line and limiting current density is shown because of concentration polarization. The η is negative for cathodic current and positive for anodic current	18
Figure 1.7 Evans diagram for iron in acid solution	21
Figure 1.8 Extrapolated Tafel curve	23
Figure 1.9 Nyquist plot along with constant phase element (CPE)	26
Scheme 2.1.1 Synthesis of Nicotinonitrile derivatives	43
Scheme 2.1.2 Synthesis of Naphthyridine derivatives	44
Scheme 2.1.3 Synthesis of Quinoline derivatives	45
Scheme 2.1.4 Synthesis of Thiopyrimidine derivatives	47
Figure 3.1.1 Effect of different concentrations of ATN and AMN on corrosion inhibition efficiency for MS in 1 M HCl	58
Figure 3.1.2 Effect of temperature (308-338 K) on corrosion inhibition efficiency for MS in presence of ATN and AMN in 1 M HCl	60
Figure 3.1.3 Langmuir adsorption isotherm plot for MS in presence of ATN and AMN	61
Figure 3.1.4 (a) Nyquist plots for MS in 1 M HCl without and with ATN and AMN	62
Figure 3.1.4 (b) Equivalent circuit model used to analyze the EIS data	62
Figure 3.1.4 (c) Bode ($\log f$ vs $\log Z $) and phase angle ($\log f$ vs α) plots for MS in 1 M HCl without and with ATN and AMN	64

Figure 3.1.5 Polarization curves for MS in 1 M HCl without and with ATN and AMN	65
Figure 3.1.6 SEM micrographs in (a) 1 M HCl and in presence of (b) ATN and (c) AMN at 0.33 mM	66
Figure 3.1.7 AFM micrographs in (a) 1 M HCl and in presence of (b) ATN and (c) AMN at 0.33 mM	67
Figure 3.1.8 The optimized molecular structures, HOMO and LUMO orbitals distribution of ATN and AMN in gas phase	69
Figure 3.1.9 Side and top views of the most stable low energy configuration for the adsorption of ATN and AMN on Fe (110) surface obtained by Monte Carlo Simulations and the density of the inhibitors distribution at the surface of iron	73
Figure 3.1.10 The adsorption energy distribution of the adsorbate (ATN and AMN molecules) on Fe (110) surface for (a) non-protonated and (b) protonated molecules	74
Figure 3.2.1 Effect of different concentrations of Naphthyridines on inhibition efficiency for MS in 1 M HCl	77
Figure 3.2.2 Effect of temperature (308-338 K) on corrosion inhibition efficiency for MS in presence of Naphthyridines in 1 M HCl	79
Figure 3.2.3 Langmuir adsorption isotherm plot for MS in presence of Naphthyridines	79
Figure 3.2.4 (a) Nyquist plots (b) Equivalent circuit model and (c) Bode-phase angle plots for MS in 1 M HCl without and with Naphthyridines	81
Figure 3.2.5 Polarization curves for MS in 1 M HCl without and with Naphthyridines at 6.54×10^{-5} M	83
Figure 3.2.6 (a-d) SEM micrographs for MS in (a) 1 M HCl and in presence of inhibitors (b) N-1, (c) N-2, and (d) N-3 at 6.54×10^{-5} M	84
Figure 3.2.7 (a-d) AFM micrographs for MS in (a) 1 M HCl and in presence of inhibitors (b) N-1, (c) N-2, and (d) N-3 at 6.54×10^{-5} M	85
Figure 3.2.8 The gas phase optimized molecular structures, the HOMO, and the LUMO electron density distribution surfaces of N-1, N-2, and N-3	86
Figure 3.2.9 The gas phase Fukui indices for the electrophilic (f_k^+) and nucleophilic (f_k^-) sites in N-1, N-2, and N-3 (isosurface value = 0.003)	89
Figure 3.2.10 A typical energy profile for the adsorption of N-3 on Fe (110) surface obtained using the Monte Carlo simulations	91

Figure 3.2.11 Side and top views of the most stable low energy configuration for the adsorption of (a) N-1, (b) N-2 and (c) N-3 on Fe (110) surface obtained by Monte Carlo Simulations	92
Figure 3.3.1 Effect of different concentrations of Quinolines on inhibition efficiency for MS in 1 M HCl	94
Figure 3.3.2 Effect of temperature (308-338 K) on inhibition efficiency for MS in presence of Quinoline derivatives in 1 M HCl	95
Figure 3.3.3 Arrhenius plots of $\log C_r$ vs. $1000/T$ for MS in the absence and presence of Quinoline derivatives at 150 mg L^{-1} in 1 M HCl	96
Figure 3.3.4 Langmuir adsorption isotherms for MS in presence of Quinoline derivatives	97
Figure 3.3.5 (a) Nyquist plots for MS without and with Quinoline derivatives in 1 M HCl	99
Figure 3.3.5 (b) Equivalent circuit model used to analyze the impedance data	99
Figure 3.3.5 (c) Bode ($\log f$ vs $\log Z $) and phase angle ($\log f$ vs α) plots of impedance spectra for MS in 1 M HCl containing Quinoline derivatives	101
Figure 3.3.6 Polarization curves for MS without and with Quinoline derivatives in 1 M HCl	102
Figure 3.3.7 SEM micrographs for MS in (a) 1 M HCl and in presence of (b) Q-1 (c) Q-2, (d) Q-3, and (e) Q-4 at 150 mg L^{-1}	104
Figure 3.3.8 AFM micrographs for MS in (a) 1 M HCl and in presence of (b) Q-1 (c) Q-2, (d) Q-3, and (e) Q-4 at 150 mg L^{-1}	105
Figure 3.3.9 The XPS deconvoluted profiles of (a) C 1s, (b) O 1s, (c) N 1s, and (d) Fe $2p_{3/2}$ for Q-4 treated MS	107
Figure 3.4.1 Effect of inhibitor concentrations (TPs) on corrosion inhibition efficiency for MS in 1M HCl	110
Figure 3.4.2 Effect of temperature (308-338 K) on inhibition efficiency for MS in presence of TPs in 1 M HCl	111
Figure 3.4.3 Arrhenius plots of $\log C_r$ vs. $1000/T$ for MS in 1 M HCl in the absence and presence of TPs at 200 mg L^{-1}	111
Figure 3.4.4 Langmuir adsorption isotherms for MS in presence of TPs	113
Figure 3.4.5 (a) The Nyquist plots for MS without and with TPs in 1 M HCl	114
Figure 3.4.5 (b) Equivalent circuit model used to analyze the impedance data	115

Figure 3.4.5 (c) Bode and phase angle plots for MS in 1 M HCl containing TPs	116
Figure 3.4.6 Polarization curves for MS without and with TPs in 1 M HCl	117
Figure 3.4.7 SEM micrographs for MS in (a) 1 M HCl and in presence of (b) TP-1 (c) TP-2 (d) TP-3 and (e) TP-4 at 200 mg L ⁻¹	119
Figure 3.4.8 AFM micrographs for MS in (a) 1 M HCl and in presence of (b) TP-1 (c) TP-2 (d) TP-3 and (e) TP-4 at 200 mg L ⁻¹	120
Figure 3.4.9 The XPS deconvoluted profiles of (a) C 1s, (b) O 1s, (c) N 1s, (d) S 2p _{3/2} and (e) Fe 2p _{3/2} for T-4 treated MS	121
Figure 3.4.10 Optimized structures of TPs	123
Figure 3.4.11 The frontier molecular orbital density distributions of TPs	124

LIST OF TABLES

Table 1.1 Classification of corrosion inhibitors	28
Table 1.2 Adsorption isotherms	32
Table 2.1.1 The molecular structures and IUPAC name of synthesized Nicotinonitrile Derivatives	43
Table 2.1.2 The molecular structures and IUPAC name of synthesized Naphthyridine derivatives	44
Table 2.1.3 The molecular structures and IUPAC name of synthesized Quinoline derivatives	46
Table 2.1.4 The molecular structures and IUPAC name of synthesized Thiopyrimidine derivatives	48
Table 3.1.1 Weight loss measurements for MS in absence and presence of ATN and AMN in 1 M HCl at 308 K	59
Table 3.1.2 ΔG_{ads} at optimum concentration (0.33 mM) of ATN and AMN for MS in 1 M HCl at 308-338 K	61
Table 3.1.3 Electrochemical impedance parameters for MS in absence and presence of ATN and AMN in 1 M HCl	64
Table 3.1.4 Polarization parameters for MS in absence and presence of ATN and AMN in 1 M HCl	65
Table 3.1.5 Quantum chemical parameters derived from the B3LYP/6-311++G** method of the studied ATN and AMN	70
Table 3.1.6 Average adsorption energy of the ATN and AMN molecules at the Fe (110) surface and the average total energy of the investigated systems	72
Table 3.2.1 Weight loss measurements for MS in absence and presence of Naphthyridines in 1 M HCl at 308 K	78
Table 3.2.2 ΔG_{ads} at optimum concentration of Naphthyridines for MS in 1 M HCl at 308-338 K	80
Table 3.2.3 Electrochemical Impedance Parameters for MS in absence and presence of Naphthyridines in 1 M HCl	82

Table 3.2.4 Polarization parameters for MS in absence and presence of Naphthyridines in 1 M HCl	83
Table 3.2.5 Quantum chemical parameters derived from the B3LYP/6-31+G (d,p) method of the studied compounds	88
Table 3.2.6 Outputs and descriptors calculated by the Monte Carlo simulation for the most stable adsorption configurations of N-1, N-2 and N-3 on Fe (110) surface (all units in kcal/mol)	91
Table 3.3.1 Weight loss measurements for MS in absence and presence of Quinoline derivatives in 1 M HCl at 308 K	95
Table 3.3.2 Activation energy for MS corrosion in absence and presence of Quinoline derivatives in 1 M HCl at 150 mg L ⁻¹	96
Table 3.3.3 ΔG_{ads} for MS in presence of Quinoline derivatives from temperature range 308-338 K at optimum concentration (150 mg L ⁻¹)	98
Table 3.3.4 Electrochemical Impedance Parameters for MS in absence and presence of Quinoline derivatives in 1 M HCl	100
Table 3.3.5 Polarization parameters for MS without and with Quinoline in 1 M HCl	103
Table 3.4.1 Weight loss measurements for MS in absence and presence of TPs in 1 M HCl at 308 K	109
Table 3.4.2 Thermodynamic parameters for MS in absence and presence of TPs in 1 M HCl at 200 mg L ⁻¹	112
Table 3.4.3 ΔG_{ads} at optimum concentration (200 mg L ⁻¹) of TPs for MS in 1M HCl at 308-338 K	113
Table 3.4.4 Electrochemical Impedance Parameters for MS in absence and presence of TPs in 1 M HCl	115
Table 3.4.5 Polarization parameters for MS in 1 M HCl containing TPs	118
Table 3.4.6 Calculated quantum chemical parameters for TPs	125
Table 3.4.7 Mulliken charges of heteroatoms present in TPs	126

ABBREVIATIONS USED

$\eta_{WL}\%$ = Percentage inhibition efficiency obtained from weight loss measurements

$\eta_{Rct}\%$ = Percentage inhibition efficiency obtained from EIS measurements

$\eta_i\%$ = Percentage inhibition efficiency obtained from Tafel measurements

C_r = Corrosion rate in uninhibited system (mm year⁻¹)

iC_r = Corrosion rate in inhibited system (mm year⁻¹)

D = Density of metal (g cm⁻³)

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

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 ($\mu F cm^{-2}$)

R_s = Solution resistance (Ωcm^2)

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

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

i_{corr} = Corrosion current density in uninhibited solution (mA cm⁻²)

$^i i_{corr}$ = Corrosion current density in inhibited solution (mA cm⁻²)

E_{corr} = Corrosion potential (mV/SCE)

A = Arrhenius pre-exponential factor (mg cm⁻² h⁻¹)

E_a = Activation energy (kJ mol⁻¹)

R = Universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)

T = Absolute temperature (K)

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

ΔG_{ads} = Gibbs free energy of adsorption (kJ mol^{-1})

θ = Degree of surface coverage of metal

C = Concentration of inhibitor (m mol, mol, mg L^{-1} , ppm)

E_{HOMO} = Energy of highest occupied molecular orbital

E_{LUMO} = Energy of lowest unoccupied molecular orbital

ΔE = Energy gap between HOMO and LUMO

ΔN = Number of electron transferred

χ_{Fe} = Electronegativity of iron

χ_{inh} = Electronegativity of inhibitor

η_{Fe} = Hardness of iron

η_{inh} = Hardness of inhibitor

f^+ = Electrophilic Fukui indices

f^- = Nucleophilic Fukui indices

PREFACE

Corrosion is inevitable process. The cost of corrosion in the industrialized countries estimates annually up to about 3-4% of the gross national product. Corrosion causes serious materials problems in many technologies and adverse effect to the environment. The need to curtail corrosion losses and introduction of highly effective methods of increasing the corrosion resistance of metallic components are constantly emphasized on considering the main directions on scientific development.

The metals used in various aggressive environments of oil industries, pipelines, refineries, domestic central heating systems, industrial cooling systems, pickling of metals, and acidization of oil well results extremely wide diversity of corrosion problems. By the available methods, such as material selection, proper designing, coating, cathodic protection, anodic protection and inhibitors the corrosion of metals can be control. The use of corrosion inhibitors is one of the effective and economic methods for corrosion control. Corrosion inhibitors are chemical compounds whose presence in adequate quantities in an aggressive medium, inhibit corrosion by bringing down corrosion rate of metal.

The first chapter introduction starts with a brief discussion about corrosion and its economic impact. The different types of corrosion, theories of corrosion and corrosion control methods have been described to explain its mechanism. A brief outline for the principle of electrode kinetics and electrochemical thermodynamics, as relevant for aqueous corrosion process is given in this chapter with discussion about the basic essentials, indispensable for the understanding of corrosion kinetics in general, and of the origins of corrosion resistance as well as of corrosion failure in particular. Special attention has been given to corrosion inhibitors among the different corrosion control methods. The techniques used to evaluate the performance of corrosion

inhibitor have been discussed in brief in this chapter. The literature survey regarding corrosion inhibitors for mild steel in acid medium has been given. The objectives of the research work have been elaborated.

The second chapter includes the details about materials and experimental techniques such as weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, surface analysis (SEM/AFM/XPS) and computational simulations have been used in the present work.

The third chapter deals with results and discussion on corrosion inhibition of mild steel in hydrochloric acid by organic corrosion inhibitors using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization. The surface morphology of mild steel in absence and presence of corrosion inhibitors have been given in this chapter. Quantum chemical calculations have been done in order to correlate various computed properties such as E_{HOMO} , E_{LUMO} , ΔE , global hardness (η), softness (σ), Mullikan charges, number of transferred electrons (ΔN) with experimentally determined inhibition efficiencies.

Major part of this thesis has been published in *Journal of Molecular Liquids* 220 (2016) 71-81, *Journal of Physical Chemistry C* 120 (2016) 3408-3419, *Journal of Molecular Liquids* 216 (2016) 164-173, and *Journal of the Taiwan Institute of Chemical Engineers* 000 (2015) 1-14.