

CONTENTS

	Page No.
CHAPTER 1	
INTRODUCTION	1- 37
1. Introduction	1
1.1. Economic losses	1
1.2. General idea of Corrosion	2
1.3. Corrosion problems in oil/petroleum industry	3
1.4. Acidizing treatment in oil wells	3
1.5. Types of Corrosion	4
(a) Chemical Corrosion or Dry Corrosion	4
(b) Electrochemical Corrosion or Wet Corrosion	5
1.6. Theories of Corrosion	6
(i) Homogeneous theory	6
(ii) Heterogeneous theory	6
(iii) Mixed potential theory	7
1.7. Thermodynamic Aspects	7
1.8. Pourbaix diagrams	10
1.9. Kinetics of Corrosion	12
1.9.1. Activation controlled corrosion	12
1.9.2. Diffusion controlled corrosion	14
1.10. Diagrams associated to Kinetic parameters	15
1.10.1. Evans Diagram	15
1.10.2. Mixed Potential Theory	16
1.10.3. Tafel Extrapolation Method	17

1.10.4. Linear Polarization Resistance	18
1.11. Electrochemical Impedance Spectroscopy	19
1.12. Corrosion Inhibitors	21
1.12.1. Definition of Inhibitor	21
1.12.2. Classification of Inhibitors	22
1.12.3. Environmental Conditions	22
1.12.4. Interface inhibitors	23
1.12.5. Vapor phase inhibitors	25
1.13. Inhibiting action of inhibitor	26
1.14. Theories of inhibition	27
1.14.1. Adsorption Theory	27
1.14.2. Film Theory	29
1.14.3. Hydrogen Overvoltage	29
1.14.4. Quantum Chemical Approach	29
1.15. Effect of inhibitors on corrosion processes	29
(a) Formation of diffusion layer	30
(b) Blocking of reaction sites	30
(c) Precipitation in the electrode reactions	30
1.16. Organic Compounds as Corrosion Inhibitors: Literature survey	31
1.17. The scope and importance of corrosion inhibition technology	36
1.18. Objective of present study	37
CHAPTER 2	
EXPERIMENTAL PROCEDURE	38-53
2. Experimental Procedure	38
2.1. Materials	38
2.1.1. Composition of Testing Material	38

2.2. Sample preparation	39
2.3. Preparation of test solutions	39
2.4. Selected inhibitors for study	39
2.4.1. Synthesis of Napthyridine derivatives	41
2.4.2. Synthesis of Pyridine derivatives	43
2.4.3. Synthesis of Isatin derivatives	45
2.4.4. Porphyrin derivatives	47
2.5. Tools	48
2.5.1 Characterization of Synthesized Compounds	48
2.6. Techniques	48
2.6.1. Corrosion rate determination by weight loss study	48
2.6.2. Electrochemical studies	49
2.7. Thermodynamic parameters determination	51
2.8. Scanning Electron Microscopy (SEM)	51
2.9. Energy dispersive X-ray Spectroscopy (EDX)	52
2.10. Contact angle measurements	52
2.11. Scanning Electrochemical Microscopy (SECM)	52
2.12. Quantum chemical calculations	52
CHAPTER 3	
RESULTS AND DISCUSSION	54-122
3.1. Napthyridine derivatives as Corrosion Inhibitors	54
3.1.1. Weight loss measurements	56
3.1.2. Thermodynamic Parameters and Adsorption Considerations	57
3.1.3. Electrochemical Impedance Spectroscopy	59
3.1.4. Potentiodynamic polarization	62
3.1.5. Surface Analysis: SEM-EDX	63

3.1.6. Quantum chemical studies	65
3.1.7. Explanation of inhibition mechanism	69
3.2. Pyridine derivatives as Corrosion Inhibitors	71
3.2.1. Weight loss measurements	73
3.2.2. Thermodynamic Parameters and Adsorption Considerations	74
3.2.3. Electrochemical Impedance Spectroscopy	76
3.2.4. Potentiodynamic polarization	80
3.2.5. Surface Analysis: SEM and SECM	81
3.2.6. Quantum chemical study	83
3.2.7. Mechanism of inhibition	87
3.3. Isatin derivatives as Corrosion Inhibitors	89
3.3.1. Weight loss measurements	91
3.3.2. Thermodynamic Parameters and Adsorption Considerations	92
3.3.3. Electrochemical Impedance Spectroscopy	94
3.3.4. Potentiodynamic polarization	97
3.3.5. Surface Analysis: SEM-EDX	99
3.3.6. Quantum chemical study	101
3.3.7. Mechanism of inhibition	104
3.4. Porphyrin derivatives as Corrosion Inhibitors	106
3.4.1. Weight loss measurements	108
3.4.2. Electrochemical Impedance Spectroscopy	108
3.4.3. Potentiodynamic polarization	112
3.4.4. Adsorption characteristics of the inhibitor	113
3.4.5. Contact Angle measurement	114
3.4.6. Scanning Electrochemical Microscopy (SECM)	115

3.4.7. Quantum chemical study	118
3.4.8. Molecular dynamic simulations	121
3.4.9. Mechanism of corrosion mitigation	122
CHAPTER 4	
SUMMARY AND CONCLUSION	123-128
4.1. Summary	123
4.2. Conclusion	127
4.3. Scope for future work	128
References	129-150
List of Publications	

List of Figures

Fig. 1.1 Corrosion cycle	1
Fig. 1.2 Formation of rust	6
Fig. 1.3 Potential-pH (Pourbaix) diagram for Fe-H ₂ O system	11
Fig. 1.4 Evans diagram	16
Fig. 1.5 (a) Anodic control (b) cathodic control, (c) mixed control	16
Fig. 1.6 A mixed potential plot for bimetallic couple of iron and zinc	17
Fig. 1.7 Extrapolated Tafel curves	18
Fig. 1.8 Hypothetical linear polarization plot	19
Fig. 1.9 A general impedance measurements curve	21
Fig. 1.10 Classifications of Inhibitors	22
Fig. 1.11 Theories of inhibition	27
Fig. 3.1.1 Variation of percentage inhibition efficiency of ANCs with temperature	57
Fig. 3.1.2 (a): Arrhenius plots of $\log C_R$ vs. $1000/T$ in absence and presence of ANCs	58
Fig. 3.1.2 (b): Langmuir's isotherm plots for adsorption of ANCs on N80 steel surface	59
Fig. 3.1.3 (a): Nyquist plots in absence and presence of optimum concentration of ANCs	60
Fig. 3.1.3 (b): Bode ($\log f$ vs. $\log Z $) and phase angle ($\log f$ vs. α°) plots in absence and presence of optimum concentration of ANCs	61
Fig. 3.1.3 (c): Equivalent circuit used to fit the EIS data	61
Fig. 3.1.4: Potentiodynamic polarization curves in absence and presence of optimum concentration of ANCs	62
Fig. 3.1.5: SEM micrographs of N80 steel (a) blank 15% HCl (b) ANC-1 (c) ANC-2 EDX spectra of N80 steel (d) blank 15% HCl (e) ANC-1 (f) ANC-2	64
Fig. 3.1.6: Optimized structures (a) ANC-1 (b) ANC-2 (c) ANC-3	65
Fig. 3.1.7: Frontier molecular orbitals of neutral (a) ANC-1 (b) ANC-2 (c) ANC-3	66

Fig. 3.1.8: Frontier molecular orbitals of protonated (a) ANC-1 (b) ANC-2 (c) ANC-3	68
Fig. 3.1.9: Plausible adsorption model of ANC-1 on to N80 steel surface in HCl	70
Fig. 3.2.1: Variation of percentage inhibition efficiency of inhibitor with temperature	74
Fig. 3.2.2 (a): Arrhenius plots of $\log C_R$ vs. $1000/T$ in absence and presence of Inhibitor	75
Fig. 3.2.2 (b): Langmuir's isotherm plots for adsorption of inhibitors	76
Fig. 3.2.3 (a): Nyquist plots in absence and presence of optimum concentration of inhibitors	77
Fig. 3.2.3 (b): Equivalent circuit used to fit the EIS data	78
Fig. 3.2.3 (c): Simulated Nyquist plot	78
Fig. 3.2.3 (d): Simulated Bode plot	79
Fig. 3.2.3 (e): Bode ($\log f$ vs. $\log Z $) and phase angle ($\log f$ vs. α°) plots in absence and presence of optimum concentration of inhibitors	79
Fig. 3.2.4: Potentiodynamic polarization curves in absence and presence of optimum concentration of inhibitors	80
Fig. 3.2.5: SEM micrographs of N80 steel (a) blank 15% HCl (b) ADP (c) AMP SECM micrographs of N80 steel (d) blank 15% HCl (e) ADP (f) AMP	82
Fig. 3.2.6: Optimized structures (a) AMP (b) ADP	84
Fig. 3.2.7: Frontier molecular orbitals (a) AMP (b) ADP	85
Fig. 3.2.8: Plausible adsorption model of AMP on to N80 steel surface in HCl	88
Fig. 3.3.1: Variation of corrosion rate with temperature	92
Fig. 3.3.2 (a): Arrhenius plots of $\log C_R$ vs. $1000/T$ in absence and presence of TZs	93
Fig. 3.3.2 (b): Langmuir's isotherm plots for adsorption of TZs on mild steel surface	94
Fig. 3.3.3 (a): Nyquist plots in absence and presence of optimum concentration of TZs	95
Fig. 3.3.3 (b): Bode ($\log f$ vs. $\log Z $) and phase angle ($\log f$ vs. α°) plots in absence and presence of optimum concentration of TZs	95
Fig. 3.3.3 (c) Simulated Nyquist plot (d) Simulated Bode plot (e) Equivalent circuit	96

Fig. 3.3.4: Potentiodynamic polarization curves for mild steel in absence and presence of optimum concentration of TZs	97
Fig. 3.3.5: SEM micrographs of mild steel (a) blank 20% H ₂ SO ₄ (b) TZ-2 (c) TZ-1 EDX micrographs of N80 steel (d) blank 20% H ₂ SO ₄ (e) TZ-2 (f) TZ-1	100
Fig. 3.3.6: Optimized structures (a) TZ-1 (b) TZ-2	101
Fig. 3.3.7: Frontier molecular orbitals of neutral (a) TZ-1 (b) TZ-2	101
Fig. 3.3.8: Frontier molecular orbitals of protonated (a) TZ-1 (b) TZ-2	102
Fig. 3.3.9: Plausible adsorption model of TZ-1 on to mild steel surface	105
Fig. 3.4.1: Variation of percentage inhibition efficiency with inhibitor concentration	108
Fig. 3.4.2 (a): Nyquist plots in absence and presence of optimum concentration of porphyrins	109
Fig. 3.4.2 (b): Equivalent circuit used to fit the EIS data	110
Fig. 3.4.2 (c): Bode ($\log f$ vs. $\log Z $) plots in absence and presence of optimum concentration of Porphyrins	111
Fig. 3.4.2 (d): Phase angle ($\log f$ vs. α°) plots in absence and presence of optimum concentration of Porphyrins	111
Fig. 3.4.3: Potentiodynamic polarization curves in absence and presence of optimum concentration of Porphyrins	112
Fig. 3.4.4: Langmuir's isotherm plots in absence and presence of optimum concentration of Porphyrins	114
Fig. 3.4.5: Contact Angle versus concentration plots for Porphyrins	115
Fig. 3.4.6: SECM (a) 3.5% NaCl x and y axis (b) 3.5% NaCl x and y axis 3D (c) P1 x and y axis (d) P1 x and y axis 3D (e) P2 x and y axis (f) P2 x and y axis 3D (g) P3 x and y axis (h) P3 x and y axis 3D	118
Fig. 3.4.7: Optimized geometries of neutral inhibitors (a) P1 (b) P2 (c) P3, Frontier molecular orbital's of neutral P1 (d) HOMO (e) LUMO, P2 (f) HOMO (g) LUMO and P3 (h) HOMO (i) LUMO	119
Fig. 3.4.8: Molecular dynamic simulations (a) P1 (b) P2 (c) P3	121
Fig. 3.4.9: Mechanism of corrosion mitigation of P1 in 3.5% NaCl solution saturated with CO ₂	122

List of Tables

Table 2.1 Composition of N80 steel (wt. %)	38
Table 2.2 Composition of mild steel (wt. %)	38
Table 2.3 Composition of J55 steel (wt. %)	38
Table 2.4 The molecular structure, abbreviations, percentage yield, spectral data (IR and NMR data of a selected compound), IUPAC name and melting points of the synthesized Napthyridine derivatives	42
Table 2.5 The molecular structure, abbreviations, percentage yield, spectral data (IR and NMR data of a selected compound), IUPAC name and melting points of synthesized Pyridine derivatives	44
Table 2.6 The molecular structure, abbreviations, percentage yield, spectral data (IR and NMR data of a selected compound), IUPAC name and melting points of synthesized Isatin derivatives	46
Table 2.7 The molecular structure, abbreviations of Porphyrin derivatives	47
Table 3.1.1 The IUPAC name, molecular structure and abbreviation of Napthyridine derivatives	55
Table 3.1.2 Corrosion parameters for the N80 steel in 15% HCl containing various concentrations of ANCs at 308 K obtained from weight loss measurements	56
Table 3.1.3 Thermodynamic parameters for the adsorption of ANCs on N80 steel at optimum concentration in 15% HCl at 308 K	58
Table 3.1.4 Electrochemical impedance parameters in absence and presence of optimum concentration (200 mg L ⁻¹) of ANCs	62
Table 3.1.5 Potentiodynamic polarization parameters in absence and presence of optimum concentration (200 mg L ⁻¹) of ANCs	63
Table 3.1.6 Calculated quantum chemical parameters of neutral and protonated ANCs	67
Table 3.2.1 The IUPAC Name, molecular structure and abbreviation of pyridine derivatives used	72
Table 3.2.2 Corrosion parameters for the N80 steel in 15% HCl containing various concentrations of inhibitors at 308 K obtained from weight loss measurements	73
Table 3.2.3 Thermodynamic parameters for the adsorption of inhibitors on N80 steel at different concentrations in 15% HCl at 308 K	76

Table 3.2.4 Electrochemical impedance parameters in absence and presence of optimum concentration (200 mg L ⁻¹) of inhibitors	77
Table 3.2.5 Potentiodynamic polarization parameters in absence and presence of optimum concentration (200 mg L ⁻¹) of inhibitors	81
Table 3.2.6 Calculated quantum chemical parameters of neutral and protonated inhibitors	85
Table 3.2.7 Mulliken charges on hetroatoms and proton affinity values	86
Table 3.3.1 The IUPAC Name, molecular structure and abbreviation of Isatin derivatives used	90
Table 3.3.2 Corrosion parameters for the mild steel in 20% H ₂ SO ₄ containing various concentrations of TZs at 308 K obtained from weight loss measurements	91
Table 3.3.3 Thermodynamic parameters for the adsorption of TZs on mild steel at optimum concentration in 20% H ₂ SO ₄ at 308 K	93
Table 3.3.4 Electrochemical impedance parameters in absence and presence of optimum (300 mgL ⁻¹) concentration of TZs	97
Table 3.3.5 Potentiodynamic polarization parameters for mild steel in absence and presence of optimum (300 mgL ⁻¹) concentrations of TZs	98
Table 3.3.6 Calculated quantum chemical parameters of neutral and protonated inhibitors	103
Table 3.4.1 The IUPAC Name, molecular structure and abbreviation of the Porphyrin derivatives used	107
Table 3.4.2 Electrochemical impedance parameters in the absence and presence of optimum concentration (400 mgL ⁻¹)	110
Table 3.4.3 The slopes of Bode impedance magnitude plots at intermediate frequencies (<i>S</i>) and the maximum phase angles (<i>αo</i>) for J55 steel in CO ₂ saturated 3.5% NaCl solution in absence and presence of optimum concentration (400 mgL ⁻¹) of Porphyrins	112
Table 3.4.4 Potentiodynamic polarization parameters in the absence and presence of optimum concentration (400 mgL ⁻¹) of Porphyrins	113
Table 3.4.5 Calculated quantum chemical parameters of neutral and protonated inhibitors	120

Symbols used

Symbols	Meaning	Units
A	Area of specimen	cm^2
C_{dl}	Double layer capacitance	$\mu\text{F cm}^{-2}$
L	Inductance	H cm^2
$\eta \%$	Percentage inhibition efficiency	--
C_R	Corrosion rate	mm year^{-1}
C_R^0	Corrosion rate in uninhibited system	mm year^{-1}
C_R^i	Corrosion rate in inhibited system	mm year^{-1}
D	Density of metal	gcm^{-3}
Y_o	Magnitude of the CPE	$\mu\text{F cm}^{-2}$
f	Frequency	s^{-1}
R_s	Solution resistance	Ω
R_{ct}	Charge transfer resistance in absence of inhibitor	$\Omega \text{ cm}^2$
$R_{ct(i)}$	Charge transfer resistance in presence of inhibitor	$\Omega \text{ cm}^2$
$-S$	Slope value of Bode impedance plot	--
$-\alpha^\circ$	Phase angle	--
I_{corr}	Corrosion current density in uninhibited solution	$\mu\text{A cm}^{-2}$
$I_{corr(i)}$	Corrosion current density in inhibited solution	$\mu\text{A cm}^{-2}$
E_{corr}	Corrosion potential	mV/ SCE
β_a	Anodic Tafel constant	mV dec^{-1}
β_c	Cathodic Tafel constant	mV dec^{-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	M^{-1}
$\Delta G^{\circ}_{\text{ads}}$	Standard free energy of adsorption	kJ mol^{-1}
θ	Degree of surface coverage	--
C	Concentration of inhibitor	mg L^{-1}
E_{HOMO}	Energy of the highest occupied molecular orbital	eV
E_{LUMO}	Energy of the lowest unoccupied molecular orbital	eV
ΔE	Energy gap	eV
t	Immersion time	h
W	Weight loss	g
h	Planck's constant	J s
R	Molar gas constant	$\text{J K}^{-1} \text{mol}^{-1}$