



Ain Shams University



Faculty of Science

Protection of petroleum equipments against corrosion and bacterial growth using novel quaternary amine inhibitors

A Thesis submitted for
The Award of the Ph.D. Degree of Science in Chemistry
By

Ahmed Hamed Mostafa Hassan

M.Sc. Inorganic Chemistry - Menoufia University (2013)

Thesis Supervisors

Prof. Dr. Galal Hosni Sayed

Prof. of Organic Chemistry, Faculty of Science, Ain Shams University

Prof. Dr. Nabel Abdel Moneem Negm

*Prof. of Petrochemicals, Petrochemicals Department
Egyptian Petroleum Research Institute*

Prof. Dr. Khalid Zakaria Selim

*Prof of Applied Physical Chemistry
Analysis and Evaluation Department
Egyptian Petroleum Research Institute*

2019



Ain Shams University



Faculty of Science

Approval Sheet

Title: - Protection of petroleum equipments against corrosion and bacterial growth using novel quaternary amine inhibitors

Name of Candidate: Ahmed Hamed Mostafa Hassan

This Thesis has been approved for submission by supervisor:-

Thesis Supervisors

Thesis approved

Prof. Dr. Galal Hosni Sayed.....

Prof. of Organic Chemistry

Faculty of Science, Ain Shams University

Prof. Dr. Nabel Abdel Moneem Negm.....

Prof. of Petrochemicals

Petrochemicals Department

Egyptian Petroleum Research Institute

Prof. Dr. Khalid Zakaria Selim.....

Prof of Applied Physical Chemistry

Analysis and Evaluation Department

Egyptian Petroleum Research Institute

Head of Chemistry Department

Faculty of Science Ain Shams University

Prof. Dr. Ayman Ayoub Abd Elshafy



Ain Shams University



Faculty of Science

Approval Sheet

Title: - Protection of petroleum equipments against corrosion and bacterial growth using novel quaternary amine inhibitors

Name of Candidate: Ahmed Hamed Mostafa Hassan

Examiners Committee

Approval

Prof. Dr. Galal Hosni Sayed

.....

Prof. of Organic Chemistry

Faculty of Science Ain Shams University

Prof. Dr. Nabel Abdel Moneem Negm

.....

Prof. of Petrochemicals

Petrochemicals Department

Egyptian Petroleum Research Institute

Prof. Dr. Mohamed Helmy Aref

.....

Prof. of Organic Chemistry

Chemistry Department

Faculty of Science Benha University

Prof. Dr. Hassan Ahmed Shehata

.....

.Prof. of Physical Chemistry

Faculty of Science- Azhar University

Head of Chemistry Department
Faculty of Science Ain Shams University
Prof. Dr. Ayman Ayoub Abd Elshafy



Ain Shams University



Faculty of Science

Approval Sheet

Title: Protection of petroleum equipments against corrosion and bacterial growth using novel quaternary amine inhibitors

Name of Candidate: Ahmed Hamed Mostafa Hassan

This Thesis has been approved for submission by supervisor:-

Thesis Supervisors

Prof. Dr. Galal Hosni Sayed

*Prof. of Organic Chemistry,
Faculty of Science, Ain Shams University*

Prof. Dr. Nabel Abdel Moneem Negm

*Prof. of Petrochemicals
Petrochemicals Department
Egyptian Petroleum Research Institute*

Prof. Dr. Khaled Zakaria Selim

*Prof of Applied Physical Chemistry
Analysis and Evaluation Department
Egyptian Petroleum Research Institute*

Thesis approved

.....

.....

.....

*Head of Chemistry Department
Faculty of Science Ain Shams University*
Prof. Dr. Ayman Ayoub Abd Elshafy



Ain Shams University



Faculty of Science

Researcher Data

Name: Ahmed Hamed Mostafa Hassan

Date of Birth: 23/08/1986

Academic Degree: MSc. Degree of Science

Field of specification: Chemistry

University issued the Degree: Menoufia University - Faculty of
Science- Chemistry Department

Graduation year: - 2007

Date of issued Degree: 2013

ACKNOWLEDGEMENT

*I am deeply thankful to almighty god for showing me the right path
and helping me to complete this work*

I wish to express my appreciation and gratitude to

Prof. Dr. Galal Hosni Sayed

Prof of Organic Chemistry

Faculty of Science

Ain Shams University

*For his interest, support, constructive criticism and fruitful discussion
through this work*

Prof. Dr. Nabel Abdel Moneem Negm

Prof. of Applied Organic Chemistry

Egyptian Petroleum Research Institute

(EPRI)

*For suggesting the research problem, guidance, advice and valuable help
throughout this work.*

Prof. Dr. Khaled Zakaria Selim

Prof of Applied Physical Chemistry

Analysis and Evaluation Department

Egyptian Petroleum Research Institute

*For suggesting the research problem, guidance, advice and valuable help
throughout this work.*

*I would like to express my sincere appreciation to my wife for her
encouragement and valuable help and support through this work*

*Finally, my special appreciation, gratefulness and thankfulness to my
Father, Mother, Brother and my Sisters.*

Contents

ABSTRACT	XV
SUMMARY AND CONCLUSION	XVI
AIM OF THE WORK	XXIV
INTRODUCTION	1
Petroleum origin	5
Crude Petroleum Oil Composition	5
Petroleum industry and its importance	6
Petroleum Processing	7
Petroleum biodegradation	8
Corrosion as a potential hazard in petroleum industry	11
Corrosion definition	13
Corrosion Processes and affecting factors	13
Basic Forms of corrosion encountered in petroleum industry	15
Sweet Corrosion	16
Sour Corrosion	17
Oxygen Corrosion	18
Galvanic Corrosion	18
Crevice Corrosion	19
Erosion Corrosion	19
Stress Corrosion Cracking	19
Microbiologically-influenced corrosion (MIC)	20
Important causes and impact of corrosion in petroleum industries	24
Production	24
Transportation and Storage	25
Refinery Operations	26
Catastrophic accidents in oil & gas industry due to corrosion	27
Corrosion Prevention and Mitigation methods	30
Material Selection	30
Design Factors	32
Protective Coatings	33

Cathodic Protection	33
Corrosion Inhibitors	34
Application of corrosion inhibitors in petroleum industries	38
Schiff's base derivatives as widespread corrosion inhibitors	40
Schiff's base derivatives as biologically active agents	54
Quaternary ammonium salts bearing Schiff's base moiety	58
Anti-corrosion activity of quaternary ammonium salts	59
Anti-bacterial activity of quaternary ammonium salts	62
EXPERIMENTAL SECTION	
Chemicals used	65
Test materials	66
Instrumentation	67
Synthesis of Schiff's base compounds	67
Synthesis of quaternary ammonium Schiff's bases	68
Measurements	68
Potentiodynamic Polarization Measurements	69
Electrochemical Impedance Spectroscopy (EIS)	69
Antimicrobial Evaluation	71
Growing of microorganisms	71
Measurements of resistance and susceptibility	71
Microorganisms	72
Minimum inhibitory concentration	72
RESULTS AND DISCUSSION	
Elemental Analyses	74
Evaluation of the prepared compounds in corrosion inhibition process	89
Potentiodynamic Polarization curves	89
Electrochemical impedance spectroscopy (EIS)	99
Electrical equivalent circuit model fitting EIS data	106

Thermodynamic considerations based on adsorption isotherm	111
Equilibrium adsorption study	112
Gibbs free energy of adsorption (ΔG_{ads}^o)	112
Mechanism of corrosion inhibition	118
Antimicrobial activity	119
Minimum inhibitory concentration	125
REFERENCES	126
ARABIC SUMMARY	

Figure No.	Title	Page
Figure 1	General Schematics of oil and gas processing installation.	8
Figure 2	The classic electrochemical corrosion cell.	15
Figure 3	Forms of CO ₂ Corrosion.	17
Figure 4	Stress corrosion cracking.	20
Figure 5	Role of SRB in the bio corrosion process of the oil pipelines.	22
Figure 6	Petroleum and some of its products	26
Figure 7	Schematic representative of the electrical cell used in the Potentiodynamic polarization measurements.	70
Figure 8	FTIR spectrum of compound AH1.	78
Figure 9a	¹ H-NMR spectrum of compound AH1.	79
Figure 9b	¹ H-NMR spectrum of compound AH1.	80
Figure 10	FTIR spectrum of compound AH2.	82
Figure 11	¹ H-NMR spectrum of compound AH2.	83
Figure 12	FTIR spectrum of compound AH3.	85
Figure 13	¹ H-NMR spectrum of compound AH3.	86
Figure 14	Polarization curves of carbon steel in 1 N H ₂ SO ₄ with or without different concentrations of the synthesized inhibitor AH4 at 25 °C.	95
Figure 15	Polarization curves of carbon steel in 1 N H ₂ SO ₄ with or without different concentrations of the synthesized inhibitor AH5 at 25 °C.	96
Figure 16	Polarization curves of carbon steel in 1 N H ₂ SO ₄ with or without different concentrations of the synthesized inhibitor AH6 at 25 °C.	97
Figure 17	Nyquist plots for carbon steel in 1 N H ₂ SO ₄ without and with different concentrations of the synthesized Inhibitor AH4.	102
Figure 18	Nyquist plots for carbon steel in 1 N H ₂ SO ₄ without and with different concentrations of the synthesized Inhibitor AH5.	103
Figure 19	Nyquist plots for carbon steel in 1 N H ₂ SO ₄ without and with different concentrations of the	104

	synthesized Inhibitor AH6.	
Figure 20	Equivalent circuit used to fit the metal/acid interface containing different concentrations of the tested inhibitors.	107
Figure 21	Bode plots for carbon steel pipelines 1N H ₂ SO ₄ without and with different concentrations of the synthesized Inhibitor AH4.	108
Figure 22	Bode plots for carbon steel pipelines 1N H ₂ SO ₄ without and with different concentrations of the synthesized Inhibitor AH5.	109
Figure 23	Bode plots for carbon steel pipelines 1N H ₂ SO ₄ without and with different Concentrations of the synthesized Inhibitor AH6.	110
Figure 24	Curves fitting the adsorption process of compound AH4 on carbon steel surface in 1 N H ₂ SO ₄ solution.	114
Figure 25	Curves fitting the adsorption process of compound AH5 on carbon steel surface in 1 N H ₂ SO ₄ solution.	115
Figure 26	Curves fitting the adsorption process of compound AH6 on carbon steel surface in 1 N H ₂ SO ₄ solution.	116

Table No.	Title	Page
Table 1	Overall elemental composition of petroleum.	6
Table 2	Reactions occurring during anaerobic Metallic corrosion in aqueous environment induced by SRB.	23
Table 3	Chemicals used in the study.	65
Table 4	Chemical composition of carbon steel used.	66
Table 5	Microelemental analysis of the prepared compounds.	75
Table 6	Electrochemical parameters obtained from polarization curves of inhibitors at 25 °C.	98
Table 7	EIS parameters for the corrosion of carbon steel in 1N H ₂ SO ₄ in absence and presence of different concentrations of AH4, AH5, and AH6 inhibitors at 25 °C.	105
Table 8	Thermodynamic parameters obtained from C_{inh}/θ and C_{inh} in 1NH ₂ SO ₄ for the adsorption of the prepared compounds AH4, AH5 and AH6 on carbon steel surface at 303 K.	117
Table 9	Antimicrobial activities ^{a, b} in terms of inhibition zone diameter at different doses (1, 2, 5 mg/mL) of the synthesized cationic Schiff's base compounds against different bacterial strains.	124
Table 10	Minimum inhibitory concentration values, MIC ^a (μM) of the synthesized cationic Schiff's base compounds against different bacterial strains.	125

In this study, three Schiff's base compounds were prepared from the reaction of o-phenylenediamine, p-phenylenediamine, and 2-aminobenzimidazole with acetophenone. The obtained Schiff's bases were quaternized using dimethyl sulfate to obtain three quaternary ammonium salts designated as AH4, AH5, and AH6. The newly synthesized quaternary ammonium salts were evaluated as corrosion inhibitors for protection of carbon steel in 1 N H₂SO₄ using different electrochemical methods, including potentiodynamic polarization and electrochemical impedance measurements at 25 °C. The adsorption of the inhibitors was obeyed Langmuir adsorption isotherm. The inhibitors were behaved as mixed type inhibitors according to their ΔG_{ads} values which were in the range of physicochemical adsorption values. The maximum inhibition efficiency was obtained using compound AH6 at concentration of 400 ppm to result an efficiency of 92.3%.

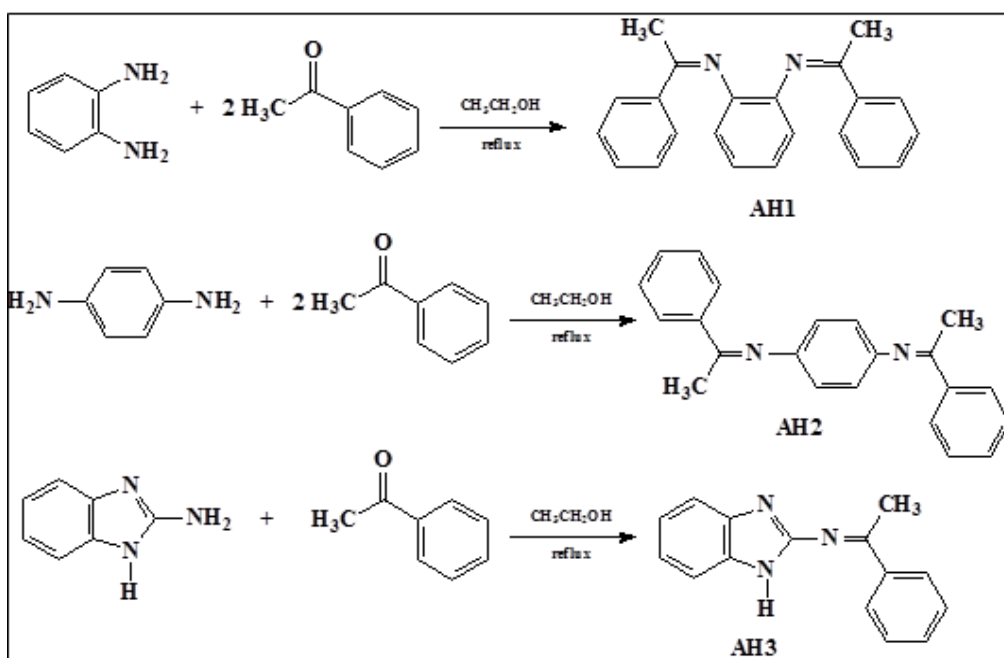
Antimicrobial evaluation of the prepared compounds showed their high inhibiting effect on Gram-positive and Gram-negative and sulfate reducing bacteria.

Keywords: Schiff's base, corrosion, adsorption, inhibition, antimicrobial evaluation.

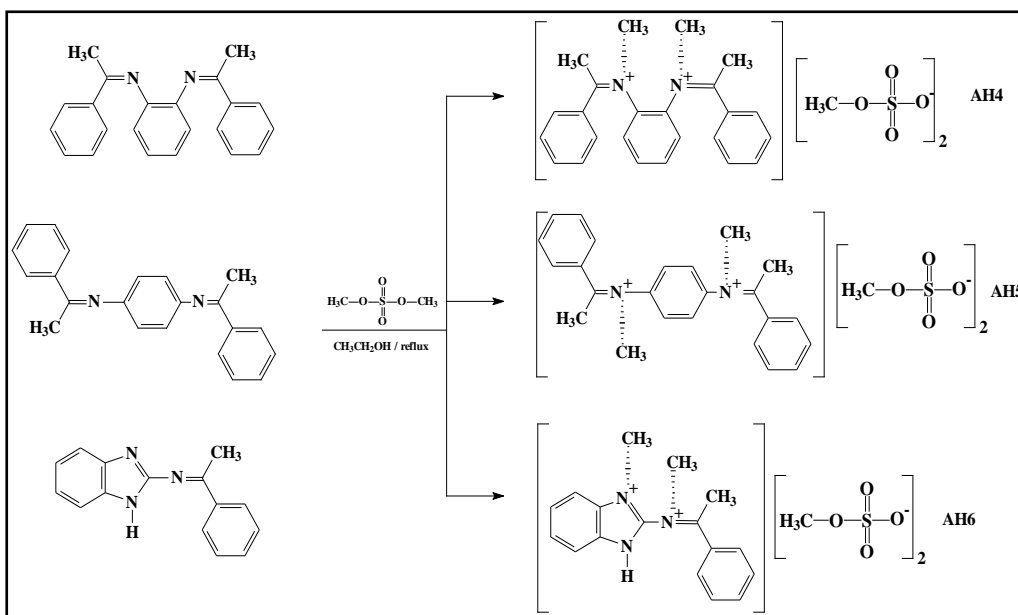
SUMMARY AND CONCLUSION

In this work, different series of Schiff's base derivatives and quaternary ammonium salts have been prepared as a corrosion inhibitor and against different bacterial growth at different conditions through the following :-

- 1- Preparation of different series from Schiff's base derivatives starting with different compounds (o-phenylenediamine, p-phenylenediamine, 2-aminobenzimidazole and acetophenone) to obtain **AH1**, **AH2**, **AH3** as showed in the following Scheme:-



- 2- Quaternization using dimethyl sulphate to obtain **AH4**, **AH5**, **AH6**.



- 3- Characterization of the prepared compounds using IR, ^1H -NMR analysis.
- 4- Studying the physicochemical properties of the prepared compounds
- 5- Evaluation of the prepared compounds as corrosion inhibitors using the electrochemical methods.
- 6- Studying the effect of the prepared compounds as corrosion inhibitor at acidic media (1 N H_2SO_4).
- 7- Antimicrobial evaluation of the prepared compounds.
- 8- Maximization of the obtained results to determine the most efficient inhibitors.

The chemical structures of the synthesized compounds were elucidated by elemental analyses, infrared spectroscopic analysis and ^1H NMR spectroscopy.