

تحضير وتقييم بعض الإضافات كمثبطات لتآكل الصلب الكربوني ومبيدات للنمو البكتيري في الاستخدامات البترولية

رسالة مقدمة من الطالب

جون ميخائيل بهيج مرقص

بكالوريوس علوم (كيمياء) - كلية العلوم - جامعة عين شمس - 2001

لاستكمال متطلبات الحصول علي درجة الماجستير
في العلوم البيئية

قسم العلوم الأساسية البيئية

معهد الدراسات والبحوث البيئية

جامعة عين شمس

2014

صفحة الموافقة على الرسالة
تحضير وتقييم بعض الإضافات كمثبطات لتآكل الصلب الكربوني ومبيدات
للنمو البكتيري في الاستخدامات البترولية

رسالة مقدمة من الطالب
جون ميخائيل بهيج مرقص
بكالوريوس علوم (كيمياء) - كلية العلوم - جامعة عين شمس . 2001

لاستكمال متطلبات الحصول علي درجة الماجستير
في العلوم البيئية
قسم العلوم الأساسية البيئية

وقد تمت مناقشة الرسالة والموافقة عليها:

اللجنة: التوقيع

1- د.أ/ماهر عبد العزيز الحشاش
أستاذ الكيمياء العضوية . كلية العلوم
جامعة عين شمس

2- د.أ/نادية غريب حسن قنديل
أستاذ الكيمياء العضوية . كلية البنات
جامعة عين شمس

3- د.أ/موازية عبد الرحمن محمد سلامة
أستاذ الكيمياء العضوية
المركز القومي للبحوث

2014

تحضير وتقييم بعض الإضافات كمثبطات لتآكل الصلب الكربوني ومبيدات للنمو البكتيري في الاستخدامات البترولية

رسالة مقدمة من الطالب

جون ميخائيل بهيج مرقص

بكالوريوس علوم (كيمياء) - كلية العلوم . جامعة عين شمس . 2001

لاستكمال متطلبات الحصول علي درجة الماجستير

في العلوم البيئية

قسم العلوم الأساسية البيئية

تحت إشراف :-

1- د.أ/ماهر عبد العزيز الحشاش

أستاذ الكيمياء العضوية . كلية العلوم

جامعة عين شمس

2- د.د/نبيل عبد المنعم نجم

أستاذ مساعد الكيمياء التطبيقية

معهد بحوث البترول

ختم الإجازة :

أجيزت الرسالة بتاريخ 2014/ /

موافقة مجلس المعهد 2014/ / موافقة مجلس الجامعة 2014/ /

2014

**SYNTHESIS AND EVALUATION OF SOME ADDITIVES AS
CORROSION INHIBITORS AND BIOCIDES FOR PETROLEUM
APPLICATION**

Submitted By

John Mikhael Bahig Morkos

B.Sc. (Chemistry), Faculty of Science, Ain Shams University, 2001

A thesis submitted in Partial Fulfillment
Of
The Requirement for the Master Degree
In
Environmental Science

Department of Environmental Basic Sciences
Institute of Environmental Studies and Research
Ain Shams University

2014

APPROVAL SHEET
**SYNTHESIS AND EVALUATION OF SOME ADDITIVES AS
CORROSION INHIBITORS AND BIOCIDES FOR PETROLEUM
APPLICATION**

Submitted By
John Mikhael Bahig Morkos

B.Sc. (Chemistry), Faculty of Science, Ain Shams University, 2001

This thesis Towards a Master Degree in Environmental Science
Has been Approved by:

Name

Signature

1-Prof. Dr. Maher Abd El Aziz El Hashash

Prof. of Organic Chemistry
Faculty of Science
Ain Shams University

2-Prof. Dr. Nadia Gharieb Hassan Kandile

Prof. of Organic Chemistry
Faculty of Girls
Ain Shams University

3-Prof. Dr. Mowafia Abd El Rahman Mohamed Salama

Prof. of Organic Chemistry
National Research Center

2014

**SYNTHESIS AND EVALUATION OF SOME ADDITIVES AS
CORROSION INHIBITORS AND BIOCIDES FOR PETROLEUM
APPLICATION**

Submitted By

John Mikhael Bahig Morkos

B.Sc. (Chemistry), Faculty of Science, Ain Shams University, 2001

A thesis submitted in Partial Fulfillment
Of
The Requirement for the Master Degree
In
Environmental Science
Department of Environmental Basic Science

Under The Supervision of:

1-Prof. Dr. Maher Abd El Aziz El Hashash

Prof. of Organic Chemistry
Faculty of Science
Ain Shams University

2-Prof. Dr. Nabel Abdel Mneem Negm

Prof. of Applied Chemistry
Egyptian Petroleum Research Institute

2014

ACKNOWLEDGEMENT

I wish to express my appreciation and gratitude to

Prof. Dr. Maher Abdel Aziz El Hashash

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

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

*The author wishes also to express his great and warm
gratitude to*

Prof. Dr. Nabel Abdel Moneem Negm

*Prof. of Applied Chemistry, Petrochemicals Department, Egyptian
Petroleum Research Institute (EPRI)*

*For suggesting the research problem, supervision,
guidance, supporting and valuable advising throughout
the steps of this work.*

*Finally, all my appreciation, gratefulness and
thankfulness to my Family and friends.*

JOHN

Contents

I. INTRODUCTION	1
Surface active agents	
1. Surfactants and their solutions	2
1.1. Definition and classification of surfactants	
1.2. Classification of surfactants	3
1.2.1. Anionic Surfactants	
1.2.1.a. Carboxylates	
1.2.1.b. Sulphate	4
1.2.1.c. Sulphonates	5
1.2.1.d. Phosphate Surfactants	6
1.2.2. Cationic Surfactants	
1.2.3. Amphoteric (Zwitterionic) Surfactants	8
1.2.4. Nonionic Surfactants	9
1.2.5. Specialty Surfactants – Fluorocarbon and Silicon Surfactants	11
1.2.6. Polymeric Surfactants	
1.2.7. Gemini surfactants	12
1.3. The hydrophobic effect and micelle formation	13
1.4. Critical micelle concentration	15
1.5. Surfactant adsorption and surface properties	16
2. Corrosion inhibition	
2.1. The Cost of Corrosion	17
2.2. Corrosion process	18
2.2.1. Cathodic Reaction	19
2.3. Forms of Corrosion	20
2.3.1. Uniform Attack	
2.3.2. Galvanic or Two-Metal Corrosion	
2.3.3. Crevice Corrosion	21
2.3.4. Pitting	22
2.3.5. Intergranular Corrosion	23
2.3.6. Selective leaching	
2.3.7. Erosion Corrosion	24
2.3.8. Stress-Corrosion Cracking	25
2.4. Classification of inhibitors	26
2.4.1. Anodic inhibitors	
2.4.2. Cathodic inhibitors	
2.4.3. Mixed inhibitors	27

CHAPTER II	
II. EXPERIMENTAL	
II.1. Chemicals	
II.2. Instrumentation	84
II.2.1. Elemental Analysis	
II.2.2. IR Spectra	
II.2.3. ¹H-NMR Spectra	
II.2.4. Tensiometer	
II.2.5. Weight	
II.2.6. Potentiostat	85
II.3. Synthesis	
II.3.1. Synthesis of 3-Aminopyridine Schiff Base	
II.3.2. Synthesis of Quaternary Ammonium Gemini Surfactants	
II.4. Measurements	86
II.4.1. Surface tension measurements (γ)	
II.4.2. Interfacial tension measurements	
II.4.3. Emulsion stability	
II.4.4. Corrosion inhibition measurements	87
II.4.4.1. Carbon Steel Composition	
II.4.4.2. Solutions	
II.4.4.3. Weight Loss Method	88
II.4.4.4. Potentiodynamic Polarization Measurements	
II.4.4.5. Electrochemical Impedance Spectroscopy (EIS)	89
CHAPTER III	
III. RESULTS AND DISCUSSION	91
III.1. Structure	
III.2. Surface activity	94
III.2.1. Surface tension-concentration relationship	96
III.2.2. Critical Micelle Concentration	98
III.2.3. Maximum Surface Excess ($\Gamma_{\max}$)	100
III.2.4. Minimum Surface Area ($A_{\min}$)	101
III.2.5. Surface tension reduction, effectiveness and efficiency (γ_{cmc}, π_{cmc}, Pc_{20})	102
III.2.6. Effect of the chemical structure on the surface activities of the surfactants	104
III.2.7. Emulsification power and interfacial tension	105
III.3. Thermodynamics of adsorption and micellization	107
III.4. Corrosion inhibition of the synthesized surfactants	109
III.4.1. Gravimetric Measurements	110
III.4.1.1. Corrosion inhibition efficiencies of the synthesized inhibitors	111
III.4.1.2. Effect of spacer chain length	
III.4.1.3. Effect of immersion time (contact time)	113

III.4.1.4. Effect of inhibitor concentration	114
III.4.1.5. Role of inhibitors in corrosion protection	118
III.4.2. Potentiodynamic polarization measurements	119
III.4.3. Electrochemical impedance measurements	125
III.4.4. Mechanism of inhibition	131
SUMMARY AND CONCLUSION	132
REFERENCES	135
Arabic summary	

List of Tables

Title	Page
The chemicals used in the study	84
Characterization of the synthesized Gemini surfactants	92
Surface activities of the Gemini surfactants at 25 °C	103
Interfacial tension and emulsification power of the Gemini synthesized surfactants at 25 °C	107
Thermodynamic properties of the synthesized Gemini surfactants at 25 °C	109
Inhibition efficiencies of the different inhibitors at 25 °C in 1 N H₂SO₄	111
Effect of spacer chain length on the surface coverage and the corrosion rates of carbon steel in the presence of different inhibitors after 24 hours in 1 N H₂SO₄	113
Effect of Immersion time on the surface coverage and the corrosion rates of carbon steel in the presence of different inhibitors after 24 hours in 1 N H₂SO₄	114
Corrosion rates of carbon steel in the presence of the different inhibitors at different concentrations after 1, 3, 6 and 24 hours immersion in 1 N H₂SO₄	116
Surface coverage of the different inhibitors at different concentrations after 1, 3, 6 and 24 hours immersion in 1 N H₂SO₄	117
Inhibition efficiencies of the different inhibitors at different concentrations in 1 N H₂SO₄	118
Polarization parameters for the corrosion process of carbon steel in 1 N H₂SO₄ containing different concentration of SB-5, SB-6, SB-10 and SB-12 inhibitors at 25 °C	124
Electrochemical impedance parameters for the corrosion of carbon steel in 1 N H₂SO₄ containing different concentration of SB-2, SB-6, and SB-12 inhibitors	130

List of Figures

Title	Page
Structure of Gemini surfactants	12
Different structures of the micelles	14
Schematic representative of the electrical cell used in the Potentiodynamic polarization measurements	90
FTIR spectra of SB-6	93
¹H-NMR spectra of SB-6	93
Surface tension vs concentration of the synthesized Gemini cationic surfactants (□: SB-2, Δ: SB-6, O: SB-12) at 25 °C	97
Relation between spacer chain length and the critical micelle concentration of the synthesized Gemini surfactants at 25 °C	99
Polarization curve of carbon steel corrosion in 1 N H₂SO₄ in the presence of different concentrations (ppm by weight) of SB-6 inhibitor at 25 °C	122
Polarization curve of carbon steel corrosion in 1 N H₂SO₄ in the presence of different concentrations (ppm by weight) of SB-12 inhibitor at 25 °C	123
Nyquist plots of carbon steel corrosion in 1 N H₂SO₄ in presence of different concentrations (ppm by weight) of SB-6 inhibitor at 25 °C	128
Nyquist plots of carbon steel corrosion in 1 N H₂SO₄ in presence of different concentrations (ppm by weight) of SB-12 inhibitor at 25 °C	129
Equivalent circuit fits the electrochemical impedance measurements	130

Abstract

The corrosion process for carbon steel is a major problem occurs in the petroleum sector. This leads to leak the oil from the pipes and tanks due to the cracks and holes occurred due to the corrosion of these instructions. That cause an environmental problem focused on the marine and the underground water. In addition the growth of anaerobic bacteria in the oil fields leads to the reduction of the sulfate ions to produce H_2S gas. That gas is very toxic and causes corrosion for the environmental units including: rocks, soils and other instructions. That type of gas is produced in high quantities due to the reduction of sulfate reducing bacteria to the sulfates in the oil wells. To avoid the two above mentioned problems, different inhibitors are used. Firstly, corrosion inhibitors are used to decrease or prevent the corrosion of the different metal fabricates. These inhibitors are either organic or inorganic. The most common type is the cationic surfactants, which have high efficiency in the corrosion prevention. The other problem due to SRB is avoided by the use of the biocides. The biocides are used widely in the petroleum sectors either to prevent or inhibit the bacterial growth, in addition to protect the cutting and drilling fluids from the degradation by bacteria.

In this work, four Schiff bases Gemini surfactants were synthesized acting as surface active agents. The chemical structures of the synthesized compounds were confirmed using elemental analysis, infrared spectroscopy (FTIR) and nuclear magnetic resonance (1H -NMR) spectroscopy. The surface activity of the synthesized compounds was investigated and showed good surface activity in their solution. The prepared compounds were evaluated as corrosion inhibitors for carbon

Abstract

steel in acidic medium using different tools: weight loss, electrochemical polarization and electrochemical impedance techniques.

- The inhibition efficiencies of the different inhibitors were increased by increasing the hydrophobic chain spacer of the Gemini cationic surfactants.
 - The presence of the heteroatoms in the rings increases the inhibition efficiencies considerably.
 - Increasing the number of positive charge in the synthesized molecule (+N) increasing the adsorption on the surface of steel and consequently increases the inhibition efficiencies.
 - Calculation of the free energy of the corrosion processes showed that the corrosion inhibitors are attached to the metal surface physically. The negative values of the free energy of adsorption of the inhibitor molecules on the metal surface indicate that their adsorption is spontaneous.
-

CHAPTER I

I. INTRODUCTION

Surface active agents

Surfactants are the major components of laundry detergents, household, and personal care products and account for over half of all use of surfactants. Interest in increasing performance in these areas has also led to research into mixed surfactant systems. Other commercial interests have also influenced the developments in surfactant science. For example in the 1970s, during the oil crisis, new methods of enhanced oil recovery, such as microemulsions, were heavily investigated. Scientific curiosity has also driven surfactant research into areas such as organization of surfactant molecules into interesting shapes and structures, all with unique properties (*Karsa et al., 1999*).

Surfactants have been the subject of investigation into the origins of life; meteorites containing lipid-like compounds have been found to assemble into boundary membranes and may be an interstellar prebiotic earth source of cell-membrane material (*Hoffman, 1994; Chevalier 2002*).

Over the past ten years, new surfactant molecules have been appearing rapidly. This growth in surfactant synthesis has, not surprisingly, paralleled the emphasis on increasing the basic performance of surfactant formulations and the provision of new surfactant technologies to a diverse range of disciplines. Although surfactant science is now a reasonably mature discipline, there is still room for new molecules designed for specific purposes and new applications (such as