



**Faculty of Science**  
**Chemistry Department**

# **"Synthesis and Evaluation of Some New Surfactants Based on Natural Material"**

*A Thesis Submitted for Degree of Ph.D. in  
Chemistry*

*By*

***Eman Abdalrahman Fathy Abdalgaleel***

(M.Sc. Organic Chemistry)

*To*

**Chemistry Department, Faculty of Science**

**Ain Shams University, Cairo, Egypt**

*Supervised by*

**Prof. Dr. Elsayed A. Soliman**

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

**Prof. Dr. Ismail A. Aiad**

Prof. of Applied Chemistry  
Petrochemicals Department,  
Egyptian Petroleum Research Institute

**Assoc. Prof. Dalia E. Mohamed**

Assoc. Prof. of Organic Chemistry  
Petrochemicals Department  
Egyptian Petroleum Research Institute

**2019**



Faculty of Science  
Chemistry Department

# "Synthesis and Evaluation of Some New Surfactants Based on Natural Material"

*A Thesis Submitted for Degree of Ph.D. in  
Organic Chemistry*

*By*

***Eman Abdalrahman Fathy Abdalgaleel***

(M.Sc. Organic Chemistry)

*To*

Chemistry Department, Faculty of Science  
Ain Shams University, *Cairo, Egypt*

*Supervised by*

**Prof. Dr. Elsayed A. Soliman**

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

**Prof. Dr. Ismail A. Aiad**

Prof. of Applied Chemistry  
Petrochemicals Department,  
Egyptian Petroleum Research Institute

**Assoc. Prof. Dalia E. Mohamed**

Assoc. Prof. of Organic Chemistry  
Petrochemicals Department  
Egyptian Petroleum Research Institute

**Head of Chemistry Department**

**Prof.Dr. Ayman Ayoub Abdel-Shafi**

**2019**

# QUALIFICATION

**Name** : Eman Abdalrahman Fathy Abdalgaleel

**Science Degree** : M.Sc.

**Department** : Chemistry

**College** : Faculty of Science

**University** : Zagazig University

**M.Sc** : 2013

## *Acknowledgement*

*First, I would like to thank “Allah” for giving me the chance and the strength to accomplish this work.*

*I would like to express my deepest gratitude, appreciation and respect to:*

***Prof. Dr. Elsayed A. soliman,** Professor of Organic Chemistry, Chemistry Department, Faculty of Science, Ain Shams University for his continuous valuable supervision, ongoing assistance and advice throughout this work.*

***Prof. Dr. Ismail A. Aiad,** Professor of Applied Chemistry, Petrochemicals Department, Egyptian Petroleum Research Institute (EPRI), for his direct supervision, valuable discussions and continuous encouragement during all phases of this work. I am grateful for his advices.*

***Dr. Dalia E. Mohamed,** Associate Professor, Petrochemicals Department, Egyptian Petroleum Research Institute, for her advice, supervision, valuable discussions, for her valuable cooperation in performing the experimental work. I am grateful for the time and efforts taken by her to read and correct the written materials and for her gentle treatment. She has supported me in every possible way since the beginning of*

*my research. Without her guidance and encouragement, my research would have never come out in the present form.*

***Dr. Emad A. Badr**, Associate Professor, Petrochemicals department, Egyptian Petroleum Research Institute (EPRI), for his valuable cooperation in performing the experimental work his valuable discussion and revision in writing. I am grateful for his advices and valuable discussions.*

*I also extend my gratitude to my lab mates, **my colleagues** who helped create a warm and friendly environment where I worked. I am indebted to all the members of Surface Active Agents Lab., Petrochemicals Department, (EPRI) Egyptian Petroleum Research Institute, especially for **Prof .Dr. ElShafie A.M.Gad** for helping me in the quantum chemical calculations part.*

# Aim of the work

This work is aimed to prepare different series of cationic surfactants based on natural material (Cinnamaldehyde, Cinnamic acid and Caffeic acid), elucidate their chemical structures, evaluate their surface activity and finally, apply them as corrosion inhibitors in oil fields. So, the main target of this thesis can be summarized as follows:

1. **Preparation** of cationic surfactants based on three compounds having natural source in plant kingdom (Cinnamaldehyde, Cinnamic acid and Caffeic acid) to obtain the following
  - N,N-dimethyl-N-(2-((3-phenylallylidene)amino)ethyl)decan-1-aminiumbromide (**Ia**)
  - N,N-dimethyl-N-(2-((3-phenylallylidene)amino)ethyl)dodecan-1-aminiumbromide (**Ib**)
  - N,N-dimethyl-N-(2-((3-phenylallylidene)amino)ethyl)hexadecan-1-aminiumbromide (**Ic**)
  - N-(2-(cinnamoyloxy)ethyl)-N,N-dimethyldodecan-1-aminium bromide (**IIa**)
  - N-(2-(cinnamoyloxy)ethyl)-N,N-dimethyldodecan-1-aminium bromide (**IIb**)
  - N-(2-(cinnamoyloxy)ethyl)-N,N-dimethylhexadecan-1-aminium bromide (**IIc**)
  - (E)-N-(2-((3-(3,4-dihydroxyphenyl)acryloyl)oxy)ethyl)-N,N-dimethyldodecan-1-aminium (**IIIa**)

- (E)-N-(2-((3-(3,4-dihydroxyphenyl)acryloyl)oxy)ethyl)-N,N-dimethyldodecan-1-aminium (**IIIb**)
  - (E)-N-(2-((3-(3,4-dihydroxyphenyl)acryloyl)oxy)ethyl)-N,N-dimethylhexadecan-1-aminium (**IIIc**)
2. **Confirmation** of the chemical structures of the synthesized compounds using FTIR, <sup>1</sup>H-NMR.
  3. **Determination** of the surface properties for the prepared surfactants and their surface parameters including surface tension, maximum surface excess, efficiency, critical micelle concentration, effectiveness, and minimum surface area.
  4. **Evaluation** of the prepared surfactants as corrosion inhibitors for carbon steel in 1M HCl solution using different techniques:
    - Weight Loss Technique
    - Potentiodynamic polarization method
    - Electrochemical impedance spectroscopy (EIS)
  5. **Determination** of quantum chemical parameters using Density Functional Theory (DFT) to correlate the experimental work to the quantum chemical calculations.

# Abstract

**Title: "Synthesis and Evaluation of Some New Surfactants Based on Natural Material ".**

*By*

*Eman Abdalrahman Fathy Abdalgaleel*

Chemistry Department, Faculty of Science, Ain Shams University

**Degree:** Doctor of Philosophy in Organic Chemistry,  
Faculty of Science, Ain Shams University, 2019.

Most of research activities interested in developing cheap, non-toxic and environmentally safe corrosion inhibitors. In this work, we focused on preparing new cationic surfactants based on cinnamaldehyde, cinnamic acid and caffeic acid which have natural source in the plant kingdom. The synthesis of the first category is carried out by two steps, The first is the condensation reaction of cinnamaldehyde with N, N-Dimethylethylenediamine in ethanol for six hours, then quaternization of the prepared Schiff base with (decyl, dodecyl and hexadecyl) bromide for 48 hours in ethanol to give products **(Ia)**, **(Ib)** and **(Ic)** with different chain length 10, 12 and 16, respectively.

The synthesis of the two categories from cinnamic and caffeic acid is carried out by esterification of these two acids with N, N-Dimethyl ethanolamine in xylene. The prepared esters 2-(dimethylamino)ethyl cinnamate/caffeate were quaternized with each of ( decyl, dodecyl and hexadecyl) bromide for 48 hours in ethanol to give products **(IIa)**, **(IIb)** and **(IIc)** with chain length



10, 12 and 16, respectively for cinnamate derivatives. While products **(IIIa)**, **(IIIb)** and **(IIIc)** with chain length 10, 12 and 16, respectively are for caffeate derivatives. The chemical structures of the prepared cationic surfactants were confirmed using FTIR and  $^1\text{H-NMR}$  spectra. The surface activity for the prepared surfactants has been studied and their surface parameters including surface tension, maximum surface excess, efficiency, critical micelle concentration, effectiveness, and minimum surface area were determined. The length of the hydrophobic chain has an effect on their surface activity as the surface tension decreases considerably by increasing their concentration and hydrophobic chain length. The prepared cationic surfactants were applied as corrosion inhibitors. The corrosion inhibition efficiency of these compounds in 1 M Hydrochloric acid on carbon steel was investigated chemically using weight loss method at different temperatures (30, 45, and 60°C) and electrochemically at 30°C using potentiodynamic polarization measurements and electrochemical impedance spectroscopy. The results reveal that, the prepared compounds **I (a-c)**, **II (a-c)**, **III (a-c)** behave as mixed type corrosion inhibitors, have significant inhibiting effect on the corrosion of carbon steel, their inhibition efficiency increased with increasing their concentration, hydrophobic chain length and the temperature. The adsorption of the studied surfactant molecules on the steel surface in Hydrochloric acid solution obeys the Langmuir adsorption isotherm. The experimental data is correlated to the theoretical calculations of quantum chemical parameters using Density Functional Theory (DFT) in order to distinguish the reactive places interacting with steel surface through the adsorption of these compounds.

**Key words:** caffeic acid; cinnamaldehyde; cinnamic acid; cationic surfactants; corrosion inhibitors and Langmuir isotherm.

## List of Contents

Topic	Page
<i>Aim of the work</i> .....	
<i>Abstract</i> .....	
<i>Chapter 1: Introduction</i>	
1. General introduction.....	1
2. Surfactants.....	4
2.1. Introduction to surfactant.....	4
2.2. Properties of surfactants.....	5
2.2.1. Adsorption .....	6
2.2.2. Micellization .....	7
2.3. Surfactants as corrosion inhibitors.....	10
2.4. Other applications of surfactants .....	12
2.4.1. Detergency .....	12
2.4.2. Surfactants as emulsifying agents .....	13
2.4.3. Food industry .....	13
2.4.4. Pharmaceutical Industry.....	14
2.4.5. Petroleum Industry .....	14
2.5. Classification of surfactants .....	15
2.5.1. Nonionic Surfactants.....	16
2.5.2. Anionic Surfactants .....	17
2.5.3. Cationic Surfactants .....	19
2.5.4. Zwitterionic Surfactants .....	20
2.6. Molecular assemblies of surfactants .....	20
3. Corrosion.....	23
3.1. Definition.....	23
3.2. Chemistry of corrosion.....	23

3.3. Types of corrosion damage .....	25
3.4. Forms of corrosion.....	25
3.5. Corrosion protection.....	27
3.6. Corrosion Inhibitors.....	28
3.6.1. Classification of inhibitors.....	23
3.6.1.1. Anodic inhibitors.....	29
3.6.1.2. Cathodic inhibitors.....	29
3.6.1.4. Mixed inhibitors .....	30
3.6.1.5. Volatile corrosion inhibitors.....	30
3.6.1.6. Precipitation inhibitors.....	31
3.6.2. Factors influencing the efficiency of corrosion inhibitors.....	31
4. Quantum chemistry .....	32
Review of literature .....	33
<b>Chapter 2: Experimental Work</b>	
1. Chemicals.....	44
2. Instruments.....	45
2.1. Fourier Transform Infrared Spectrometer (FTIR).....	45
2.2. Proton Nuclear Magnetic Resonance ( <sup>1</sup> HNMR).....	45
2.4. Tensiometer.....	45
2.5. Potentiostat.....	45
3. Synthesis .....	45
3.1. Synthesis of imine cationic surfactants based on Cinnamaldehyde	45
3.1.1. Schiff Base Preparation.....	46
3.1.2. Quaternization of the prepared Schiff Base .....	46
3.2. Synthesis of cationic surfactants based on Cinnamic and Caffeic acid .....	46
3.2.1. Esterification reaction .....	46
3.2.2. Quaternization reaction .....	47

4. Measurements .....	48
4.1. Surface Tension Measurements ( $\gamma$ ) .....	48
4.2. Corrosion measurements.....	50
4.2.1. Weight loss measurements.....	50
4.2.2. Potentiodynamic polarization method .....	52
4.2.3. Electrochemical impedance spectroscopy (EIS).....	53
4.3. Computational Methodology.....	55
<b>Chapter 3: Results and discussion</b>	
3.1. Synthesis.....	56
3.2. Structure confirmation .....	61
3.2.1. Fourier Transform Infrared spectra (FTIR).....	61
3.2.2. Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ).....	68
3.3. Surface parameters for the prepared cationic surfactants.....	74
3.3.1. Surface tension ( $\gamma$ ).....	74
3.3.2. Critical micelle concentration (CMC) .....	79
3.3.2. Effectiveness ( $\pi_{\text{cmc}}$ ).....	81
3.3.4. Efficiency ( $\text{Pc}_{20}$ ).....	81
3.3.5. Maximum surface excess ( $\Gamma_{\text{max}}$ ).....	82
3.3.6. Minimum surface area ( $A_{\text{min}}$ ) .....	84
3.4. Corrosion measurements .....	86
3.4.1. Weight loss measurements.....	86
3.4.1.1. Effect of concentration of the inhibitors .....	86
3.4.1.2. Effect of hydrophobic chain length.....	87
3.4.1.3. Effect of hydrophilic group (head group).....	87
3.4.1.4. Effect of Temperature .....	88
3.4.2. Potentiodynamic polarization measurements.....	105
3.4.3. Electrochemical impedance spectroscopy (EIS).....	70

## ***Contents***

---

3.5. Adsorption isotherm and standard adsorption free energy.....	78
3.6. Activation energy.....	
3.7. Mechanism of corrosion inhibition.....	153
3.8. Quantum chemical calculations.....	
<b><i>Summary and conclusions</i></b> .....	
<b><i>References</i></b> .....	174
<b><i>Arabic summary</i></b> .....	

***List of Figures***

<b>Figure No.</b>	<b>Title</b>	<b>Page</b>
1	Schematic illustration of a surfactant .....	4
2	Effect of surfactant on the surface tension .....	5
3	Surfactants adsorption at the surface.....	7
4	Plot of surface tension versus log conc. showing cmc..	8
5	Adsorption of surfactant on steel surface.....	11
6	Surfactants classification according to the composition of their head.....	16
7	Schematic representations of organized aggregates that may form in aqueous solution of surfactant depending on the concentration.....	22
8	Corrosion process on metal surface.....	24
9	Standard electrochemical cell.....	54
10	The working electrode.....	54
11	FTIR spectra of the prepared cationic surfactants <b>(Ia)</b> , <b>(Ib)</b> and <b>(Ic)</b> .....	65
12	FTIR spectra of the prepared cationic surfactants <b>(IIa)</b> , <b>(IIb)</b> and <b>(IIc)</b> .....	66
13	FTIR spectra of the prepared cationic surfactants <b>(IIIa)</b> , <b>(IIIb)</b> and <b>(IIIc)</b> .....	67
14	<sup>1</sup> H-NMR spectra of the prepared cationic surfactants <b>(Ia)</b> , <b>(Ib)</b> and <b>(Ic)</b> .....	71
15	<sup>1</sup> H-NMR spectra of the prepared cationic surfactants <b>(IIa)</b> , <b>(IIb)</b> and <b>(IIc)</b> ... ..	72
16	<sup>1</sup> H-NMR spectra of the prepared cationic surfactants	

	<b>(IIIa), (IIIb) and (IIIc)</b> .....	73
17	Variation of the surface tension with log conc. for the prepared surfactants <b>(Ia, Ib and Ic)</b> at room temperature .....	76
18	Variation of the surface tension with log conc. for the prepared surfactants <b>(IIa, IIb and IIc)</b> at room temperature.....	76
19	Variation of the surface tension with log concentrations for the prepared surfactants <b>(IIIa, IIIb and IIIc)</b> at room temperature.....	77
20	The relation between corrosion inhibition efficiency of carbon steel and logarithm of the concentration of the inhibitors <b>(Ia, Ib and Ic)</b> .....	93
21	The relation between temperature and the inhibition efficiency of the prepared inhibitors <b>(Ia, Ib and Ic)</b> at different concentrations obtained by weight loss method for carbon steel in 1.0 M HCl.....	94
22	The relation between corrosion inhibition efficiency of carbon steel and logarithm of the concentration of the inhibitor <b>(IIa, IIb and IIc)</b> .....	98
23	The relation between temperature and the inhibition efficiency of the prepared inhibitors <b>(IIa, IIb and IIc)</b> at different concentrations obtained by weight loss method for carbon steel in 1.0 M HCl.....	99
24	The relation between corrosion inhibition efficiency of carbon steel and logarithm of the concentration of the inhibitor <b>(IIIa, IIIb and IIIc)</b> .....	103
25	The relation between temperature and the inhibition	