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
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Petrochemicals Department,
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2019

QUALIFICATION

Name : Eman Abdalrahman Fathy Abdalgaleel

Science Degree : M.Sc.

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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-dimethyldecan-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-dimethyldecan-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, ^{1}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

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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 cinnmaldehyde 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}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^{o}C) and electrochemically at 30^{o}C using potentiodynamic polarization measurements and electrochemical impedence 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.

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