Ain Shams University
Faculty of Science
Department of Chemistry

"Synthesis and evaluation of some new cationic surfactants as corrosion inhibitors for carbon steel pipelines in oil and gas production"

A Thesis Submitted By

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This thesis has been approved for submission by the supervisors:

Prof. Dr. / Sayed Sabet Abd El Rehim

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Prof. Dr / *Mohamed Abd El Azim Hegazy*

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APPROVAL SHEET FOR SUBMISSION

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Candidate

Ahmed Hussien Ahmed Youssif

Dedication

*To my lovely **father** and **mother** with my deep and sincere appreciation for their great efforts during my life and my studies.*

*To my darling **wife** and **children** for supporting.*

*To my **sisters** and **brother** with my great thanks for their help.*

Ahmed Hussein

List of Abbreviations

Symol. List	**Abbreviation Name**
A	Arrhenius constant
A_{min}	Minimum Surface Area
C	The concentration of surfactant
C_{dl}	Double layer capacitance
CE	Counter electrode
C_{cmc}	Critical Micelle Concentration
CP	Cathodic protection
CPE	Constant phase element
E_a	The activation energy of the metal dissolution reaction
E_{corr}	The corrosion potentials
EIS	Electrochemical Impedance Spectroscopy
f	impedance frequency
FTIR	Fourier transform-Infra red
GNP	Gross National Products
^{1}HNMR	Hydrogen proton nuclear magnetic resonance
i_{corr}	The corrosion current density values in the presence of the inhibitors
i^{o}_{corr}	The corrosion current density values in the absence of the inhibitors
K	Corrosion rate of carbon steel
K_{ads}	The equilibrium constant for adsorption desorption process

LP	Linear polarization
LPR	linear polarisation resistance
M. wt	Molecular weight
MIC	Microbial Induced Corrosion
mpy	Mille inch per year
n	Phase shift
N_A	The Avogadro's number
OCP	Open circuit potential
PZC	Potential of zero charge
R	The gas constant
R_{ct}	Charge transfer resistance values with inhibitor
RE	Reference electrode
R^o_{ct}	Charge transfer resistance values without inhibitor
R_p	Polarization resistance
R_s	Solution resistance
S	The total area of the specimen
SACP	Sacrificial anode corrosion protection
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
SI	Synergistic effect
SRB	Sulfate Reducing Bactria
SS	Stainless Steel
T	The absolute temperature

t	The immersion time of specimen in solution
U.S	United states
VCIs	Volatile corrosion inhibitors
W	The weight loss of carbon steel in the presence of the inhibitors
WE	Working electrode
W_o	The weight loss of carbon steel in the absence of the inhibitors
Z_{img}	Frequency at maximum imaginary component
β_a	The anodic Tafel slope
β_c	The cathodic Tafel slope
γ_{cmc}	Surface tension of surfactants at C_{cmc} of surfactant ions
γ_o	Surface tensions of pure water
ΔG^o_{asd}	The free energy of adsorption process
ΔG^o_{mic}	Change free energy of micellization
ΔH^*	Activation enthalpy
ΔH^o_{ads}	The enthalpy of adsorption process
ΔS^*	Activation entropy
ΔS^o_{ads}	The entropy of adsorption process
η_w	The corrosion inhibition efficiency
π_{CMC}	Effectiveness (surface pressure)
Θ	The surface coverage of inhibitor on carbon steel
ω	Angular frequency
%IE	Inhibition efficiency

Γ_{max}	Maximum Surface Excess

Aim of the Work

The main targets of this work are:

1. Synthesis of some cationic surfactants

Preparation of cationic surfactants by reaction of $N^1,N^{1'}$-(ethane-1,2-diyl)bis(ethane-1,2-diamine) with isonicotinaldehyde followed by quaternization reaction with fatty alkyl bromide to obtain the desired surfactants:

- N-(2-((E)-(pyridin-4-ylmethylene)amino)ethyl)-N-(2-((2-((Z)-(pyridin-4-ylmethylene)amino)ethyl)amino)ethyl) dodecan-1-aminium bromide I(4N).
- N^1,N^2-didodecyl-N^1-(2-((E)-(pyridin-4-ylmethylene)amino) ethyl)-N^2-(2-((Z)-(pyridin-4-ylmethylene) amino)ethyl)ethane-1,2-diaminium bromide II(4N).
- 4,4'-((1Z,11E)-5,8-didodecyl-2,5,8,11-tetraazadodeca-1,11-diene-5,8-diium-1,12-diyl)bis(1-dodecylpyridin-1-ium) bromide IV(4N).

2. Structure elucidation

Structure conformation of the synthesized Schiff base and surfactants using different spectroscopic techniques:

- FT-IR spectroscopy.
- ^{1}HNMR spectroscopy.
- Mass spectroscopy.

3. Determination of the physical properties:

Determination of surface properties for prepared surfactants and thermodynamic parameters of the micelle formation.

4. Application:

Evaluation of prepared surfactants as corrosion inhibitors for carbon steel in 1M HCl solution and formation water using different techniques:

- Weight Loss.
- Potentiodynamic polarization.
- Electrochemical impedance spectroscopy (EIS).

Summary

The work discusses the corrosion inhibition of carbon steel metal in 1M HCl solution and formation water by different synthesized cationic surfactants I(4N), II(4N) and IV(4N). In this work, the inhibition effects of those compounds have been studied by several experimental methods.

This work contains three chapters:

Chapter 1:"Introduction"

This chapter includes a general introduction about corrosion (definition, the economic cost, forms, factors, prevention and types of inhibitors) and surfactants (definition, classification and applications).

Chapter 2: "Materials and experimental techniques"

The experimental part includes complete description of chemicals used, preparation of solutions, metal composition, synthesis of cationic surfactants and description of their application as the following:

- Synthesis of new cationic surfactants

The desired cationic surfactants were synthesized through two main steps, the first step was formation of the main Schiff base by reaction $N^1,N^{1'}$-(ethane-1,2-diyl)bis(ethane-1,2-diamine) with isonicotinaldehyde while the second step was quaternization reaction of the prepared Schiff base with different number of

dodecyl bromide compounds to obtain the desired cationic surfactants.

- Confirmation the chemical structure of prepared Schiff base and cationic surfactants using FTIR, ^{1}HNMR and Mass spectroscopes.
- Evaluation the inhibition efficiency for the synthesized cationic surfactants as corrosion inhibitors for carbon steel pipelines in both 1M HCl solution and formation water by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques.
- Determination of activation and adsorption thermodynamic parameters of the cationic surfactants on the carbon steel surface in 1M HCl solution and formation water.
- Determination of synergistic effect between KI, $ZnCl_2$ and the cationic surfactants in formation water.

- Determination of the surface parameters of the synthesized cationic surfactants.

Chapter 3: "Results and discussion"

This chapter included the following parts:-

1. **Characterization of the synthesized Schiff bases:**

The chemical structure of the synthesized cationic surfactants was confirmed by spectroscopy analysis include: FTIR, ^{1}HNMR, and Mass Spectra.

2. **Evaluating of the synthesized cationic surfactants as corrosion inhibitors for carbon steel in 1M HCl solution and formation water by**

    2.1. Weight loss measurements

The prepared compounds I(4N), II(4N) and IV(4N) were tested as corrosion inhibitors for carbon steel in 1M HCl solution at four different temperatures 25, 40, 55 and 70^{o}C and in formation water at 25^{o}C only. The data revealed that, the inhibition efficiency of the synthesized cationic surfactants increases with increasing the cationic surfactant concentration in both media, also it was found that inhibition efficiency decreases with increasing the temperature in 1M HCl.

Synergistic effect between KI, $ZnCl_2$ and cationic surfactants in formation water was studied. The experimental data showed that, after adding various concentrations of KI and $ZnCl_2$ to the cationic surfactants at 25 ^{o}C, the inhibition efficiency increases by increasing the concentration of inorganic salts. This behaviour indicating that, the synergism phenomenon exists between cationic surfactant and KI or $ZnCl_2$ leading to increasing the inhibition efficiency

2.2. Potentiodynamic polarization measurements

The data indicated that:-

The presence of the synthesized cationic surfactants in both 1M HCl solution and formation water slightly shifted the corrosion potential (E_{corr}) to both negative and positive directions. This indicates that the synthesized cationic surfactants acted as a mixed type inhibitor

For all synthesized cationic surfactants,(i_{corr}) decreased whereas (η_p) increased with increasing the inhibitor concentration. This could be related to the adsorption of the inhibitor over the cathodic and anodic active corroded surface. The increase in corrosion inhibition efficiency of the studied surfactant indicated that the synthesized cationic surfactant had efficient inhibitive properties for the metal surface.

2.3. Electrochemical impedance spectroscopy (EIS)

In both 1M HCl solution and formation water, the data showed that the increase of charge transfer resistance (R_{ct}) and decrease of the pseudo capacity, (C_{dl}), with increasing the inhibitor concentration indicated that, these compounds have the ability to