Ain Shams University Faculty of Science Department of Chemistry



"Preparation and Characterization of Some Cationic Surfactants Capped Metal Nanoparticles and Their Applications"

A Thesis Submitted for Degree of Ph.D. in Organic Chemistry
To Department of Chemistry – Faculty of Science
Ain Shams University

By

Samy Mohamed Ahmed Shaban

(M.Sc., 2009)
Department of Chemistry - Faculty of Science
Zagazig University

APPROVAL SHEET FOR SUBMISSION

Title of Thesis: Preparation and Characterization of Some Cationic Surfactants Capped Metal Nanoparticles and Their Applications"

Name of the Candidate: Samy Mohamed Ahmed Shaban

This thesis has been approved for submission by the supervisors:

Prof. Dr. /El-Sayed Ahmed Soliman

Signature:

Prof. Dr. / Mohammed Abd-El Rahman El-Sukkary

Signature:

Prof. Dr. /Ismail Abd-El Rahman Aiad

Signature:

Ass.Prof. Dr/ Moshira ELawady

Signature:

Head of Chemistry Department.

Faculty of Science- Ain Shams University.

Prof. Dr.\ Hamed Ahmed younis drbalah

ACKNOWLEDGMENT

At the beginning, I would like to thank "Allah" for giving me the opportunity and the strength to accomplish this work.

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

Prof. Dr. Sayed Ahmed soliman, Prof. of organic chemistry, Faculty of Science, Ain Shams University, for his supervision pleasant guidance and continuous encouragement during the research.

Prof. Dr. Mohamed EL Sukkarry, Prof. of Applied Organic Chemistry, Egyptian Petroleum Research Institute, for his valuable advice, talented supervision, and constructive criticism during the progress of the work.

Prof. Dr. Ismail Abd El Rahman Aiad, Prof. of Applied chemistry, Egyptian Petroleum Research Institute, for his guidance in selecting the research point, close supervision, and valuable advice throughout the work.

Ass. Prof. Dr. Moshira ELawady, Ass. Prof of Organic Chemistry, Petrochemicals Department, Egyptian Petroleum Research Institute, for her continuous guidance and valuable advice.

Finally, I would like to thank my colleagues and all members of Petrochemicals department, EPRI, especially the members of Surface Active Agents Lab., for providing the facilities to carry out the practical part of this work.

Samy Mohamed Ahmed Ibrahim Shabaan

إهراء

أهدي هذه الرسالة إلى روح والدي رحمه الله وأسأل الله العظيم أن يتغمده بواسع رحماته وإلى أمى الحبيبة وإلى زوجتي

CONTENTS

•	Abbreviation		
List of Tables			
_	List of Figures List of Shemes		
List oj Abstra			
CHAPT!			
CATI:	EX(1:		
1. INTR	ODUCTION SECTION		
1.1. Su	urfactants	1	
	Media	4	
1.1.2. Cl	assification of surfactants	8	
1.1.3. A	pplications of surfactants	28	
1.2. Co	orrosion	35	
1.2.1.	Definition of Corrosion	35	
1.2.2.	Corrosion Protection	39	
1.3.	Nano Science	43	
1.3.1.	Metal Nanoparticles	46	
1.3.2.	The role of surfactants in nanoparticles formation	48	
1.3.3.	Applications of Metal Nanoparticles	51	

1 4 1 17		=
1.4. LII	ERATURE REVIEW	53
1.4.1.	Surface Parameters of Surfactants	53
1.4.2.	Surfactants as Corrosion Inhibitors	60
1.4.3.	Nano-Technology	66
1.4.4.	Aim of the Work	74
СНАРТІ	ER 2:	
2. <i>Expe</i>	erimental Section	
2.1. Ch	emicals Used	77
-	nthesis of Cationic Surfactants and Silver noparticles	78
2.2.1.	Preparation of Cationic Surfactants	78
2.2.2.	Preparation of Silver Nanoparticles	79
2.3. Str	uctural Confirmation of Prepared Compounds	81
2.3.1.	Structure Confirmation of Prepared Cationic Surfactants	81
I.	Fourier Transform Infrared Spectrometer (FTIR)	81
II.	¹ H-NMR Spectroscopy	81
III.	Mass spectroscopy	81
2.3.2.	Confirmation of silver nanoparticle formation	82

	I.	Transmission Electron Microscope (TEM)	82
	II.	UV- Visible Spectroscopy	82
	III.	Dynamic Light Scattering (DLS) and Zeta Potential Measurements	83
	IV	. Energy Dispersive X-ray (EDX) spectroscopy	83
	V.	Fourier Transform Infrared Spectrometer (FTIR)	84
2.4.	Me	easurements	84
2.4	4.1.	Surface Tension Measurements (γ)	84
2.4	4.2.	Corrosion Measurements	85
	2.4	.2.1. Weight Loss Method	85
	2.4	.2.2. Potentiodynamic Polarization Method	87
	2.4	.2.3. Electrochemical impedance spectroscopy (EIS)	90
2.4	4.3.	Biological activity	90
	2.4	3.1. Biological activity against a wide range of bacteria and fungi	90
	2.4	Bacteria. Biocidal activity against Sulfate reducing	93
СНЯ	1PTI	ER 3:	
3. R	ESU	LTS and DISCUSSION	
3.1.	Syn	thesis of Cationic Surfactants	95

3.2. Structure Confirmation of the Synthesized Surfactants	100
3.2.1. Fourier Transfer Infrared Spectroscopy (FTIR)	100
3.2.2. ¹ H-NMR Spectra	116
3.2.3. Mass Spectra	136
3.3. Synthesis of Silver Nanoparticles	144
3.3.1. Formation Mechanism of Silver Nanoparticles	145
3.3.2. Confirmation of Silver Nanoparticle Formation	149
3.3.2.1. Transmission Electron Microscope (TEM) and Selected Area Electron Diffraction (ED)	149
3.3.2.2. UV- Vis Spectroscopy	163
3.3.2.3. Dynamic Light Scattering (DLS)	174
3.3.2.4. Energy Dispersive X-ray (EDX)	185
3.3.2.5. FT-IR spectroscopy	188
3.4. Surface Activities of Prepared Cationic Surfactants	192
3.4.1. Surface Tension (γ)	192
3.4.2. Critical Micelle Concentration of Prepared Cationic Surfactants (CMC)	207
3.5. Thermodynamic Parameters of Micellization and Adsorption of Prepared Cationic Surfactants	222

Contents

3.6. Stud	lying the Corrosion Inhibition of C-Steel in1M	
Hyd	Hydrochloric acid by New Cationic surfactants	
3.6.1.	Gravimetrical Evaluation of the Synthesized	220
	Inhibitors	230
3.6.1.1.	Effect of Inhibitor Concentrations	230
3.6.1.2.	Effect of Temperature	232
3.6.1.3.	Effect of Hydrophobic Chain Length	234
3.6.1.4.	Effect of Hydrophilic group (head group)	235
3.6.2.	Potentiodynamic Evaluation of the Synthesized	260
	Inhibitors	260
3.6.3.	Electrochemical Impedance Spectroscopy (EIS)	279
3.6.4.	Activation Thermodynamic Parameters of	
	corrosion process in 1M HCl	299
3.6.5.	Adsorption Isotherm	323
3.7. Ev	valuation of the synthesized surfactants as	
	antibacterial and antifungal	337
4. Summary and Conclusion		352
5. Refe	5. References	

List of Abbreviation

Symol.	Abbreviation Name	Unit
γ	Surface Tension	mN/m^{-1}
CMC	Critical Micelle Concentration	mM/L
Γ_{max}	Maximum Surface Excess	mol.cm ⁻²
A_{\min}	Minimum Surface Area	A^2
π_{CMC}	Effectiveness	mNm^{-1}
PC_{20}	Efficiency	
$\Delta G^{\it o}_{\it mic}$	Change free energy of micellization	Kj mol ⁻¹
ΔG^{o}_{ads}	Change free energy of adsorption	Kj mol ⁻¹
ΔH_{mic}	Change in enthalpies of micellization	Kj mol ⁻¹
ΔH_{ads}	Change in enthalpies of adsorption	Kj mol ⁻¹
ΔS_{mic}	Change in entropy of micellization	Kj mol ⁻¹ K ⁻¹
ΔS_{ads}	Change in entropy of adsorption	Kj mol ⁻¹ K ⁻¹
CR	Corrosion rate of carbon steel	mg/cm ² .h
W	weight loss	mg
S	Area of mild steel species	Cm^2
t	time of immersion	hrs
I_{Corr}	Corrosion current densities	mA cm ⁻²
β_a	Anodic Tafel slope	mV dec ⁻¹
β_c	Cathodic Tafel slope	mV dec ⁻¹
E_{corr}	Corrosion potential	mV

List of Abbreviation

$R_{\rm s}$	Solution resistance	ohm cm ²
R_{ct}	Charge transfer resistance	ohm cm ²
C_{dl}	Double layer capacitance	μF cm ⁻²
$Z^{''}_{\mathrm{img}}$	Frequency at maximum imaginary component	Hz
Ea	Activation Energy	kJ mol ⁻¹
ΔH^*	The change in enthalpy of activation	kJ mol ⁻¹
ΔS^*	The change in entropy of activation	J mol ⁻¹ K ⁻¹
θ	Surface coverage	
η	Efficiency of inhibition	
TEM	Transmission Electron Microscope	
DLS	Dynamic Light Scattering	
EDX	Energy Dispersive X-ray spectroscopy	
EIS	Electrochemical impedance spectroscopy	
SRB	Sulfate reducing Bacteria	
AgNPs	Silver Nanoparticles	

List of Tables

No.	Table Name	page
1:1	Types of disperse systems in pharmaceutical	30
	formulations.	
2:1	The chemicals used and their sources and grades.	77
3:1	Characteristic peaks of prepared cationic surfactants.	102
3:2	Size distribution of prepared silver nanoparticles	175
	using prepared capping agents.	
3:3	Zeta Potential and conductivity of prepared silver	184
	nanoparticle by dynamic light Scattering (DLS).	
3:4	Surface Parameters of Synthesized Cationic	220
	Surfactants at Different Temperatures.	
3:5	Thermodynamic Parameters of Micellization of	225
	Synthesized Cationic Surfactants at Different	
	Temperatures.	
3:6	Thermodynamic Parameters of Adsorption of	
	Synthesized Cationic Surfactants at Different	227
	Temperatures.	
3:7	Weight loss results of carbon steel corrosion without	
	and with different concentrations of C10V at	236
	different temperatures.	
3:8	Weight loss results of carbon steel corrosion without	238
	and with different concentrations of C12V at	

	different temperatures.	
3:9	Weight loss results of carbon steel corrosion without	240
	and with different concentrations of C16V at	
	different temperatures.	
3:10	Weight loss results of carbon steel corrosion without	242
	& with different concentrations of C10Bn at	
	different temperatures.	
3:11	Weight loss results of carbon steel corrosion without	
	& with different concentrations of C12Bn at	244
	different temperatures.	
3:12	Weight loss results of carbon steel corrosion without	
	& with different concentrations of C16Bn at	246
	different temperatures.	
3:13	Weight loss results of carbon steel corrosion without	248
	& with different concentrations of C10Dim at	
	different temperatures.	
3:14	Weight loss results of carbon steel corrosion without	250
	& with different concentrations of C12Dim at	
	different temperatures.	
3:15	Weight loss results of carbon steel corrosion without	252
	& with different concentrations of C16Dim at	
	different temperatures.	
3:16	Weight loss results of carbon steel corrosion without	254

	& with different concentrations of C10B1 at	
	different temperatures.	
3:17	Weight loss results of carbon steel corrosion without	256
	& with different concentrations of C12BTat	
	different temperatures.	
3:18	Weight loss results of carbon steel corrosion without	258
	& with different concentrations of C16BTat	
	different temperatures.	
3:19	Potentiodynamic polarization parameters for	
	corrosion of carbon steel in 1M HCl in absence	
	and presence of different concentrations of	263
	synthesized cationic surfactants C10V, C12V	
	and C16V at 25°C at scanning rate 2 mV s ⁻¹ .	
3:20	Potentiodynamic polarization parameters for	
	corrosion of carbon steel in 1M HCl in absence	267
	and presence of different concentrations of	
	synthesized cationic surfactants C10Bn, C12Bn	
	and C16Bn at 25°C at scanning rate 2 mV s ⁻¹ .	
3:21	Potentiodynamic polarization parameters for	
	corrosion of carbon steel in 1M HCl in absence	
	and presence of different concentrations of	271
	synthesized cationic surfactants C10Dim,	
	C12Dim and C16Dim at 25°C at scanning rate 2	

 $mV s^{-1}$.

3:22	Potentiodynamic polarization parameters for	
	corrosion of carbon steel in 1M HCl in absence	
	and presence of different concentrations of	275
	synthesized cationic surfactants C10BT, C12BT	
	and C16BT at 25°C at scanning rate 2 mV s ⁻¹ .	
3:23	EIS parameters for corrosion of carbon steel in 1M	
	HCl in the absence and presence of different	283
	concentrations of of synthesized cationic	
	surfactants C10V, C12V and C16V at 25°C	
3:24	EIS parameters for corrosion of carbon steel in 1M	
	HCl in the absence and presence of different	
	concentrations of of synthesized cationic	287

3:25 EIS parameters for corrosion of carbon steel in 1M HCl in the absence and presence of different concentrations of of synthesized cationic 291 surfactants C10Dim, C12Dim and C16Dim at 25°C.

surfactants C10Bn, C12Bn and C16Bn at 25°C.

3:26 EIS parameters for corrosion of carbon steel in 1M

HCl in the absence and presence of different 295

concentrations of of synthesized cationic

surfactants C10BT, C12BT and C16BT at 25°C