

**A STUDY ON SOME APPLICATIONS  
FOR SOME  
SURFACE-ACTIVE AGENTS**

Thesis

Submitted For the Degree of  
Doctor of Philosophy

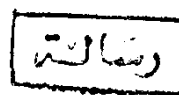
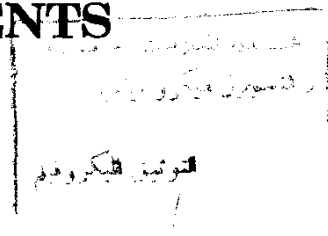
In  
Chemistry

BY

*Muhammad*  
**SANAA ABO EL FOTOUH EL KHOLY**

Chemistry Department  
Faculty of Women  
AIN SHAMS UNIVERSITY

1993



**Ain Shams University  
Faculty of Women  
Chemistry Department**

**Ph.D. Thesis  
(CHEMISTRY)**

**A STUDY ON SOME APPLICATIONS FOR  
SOME SURFACE-ACTIVE AGENTS**

**Thesis Supervisors:**

- **Prof. Dr. MOHAMED FAROUK EZZAT**
- **Prof. Dr. NADIA ABD EL HAKEM YOUSSEF**
- **Prof. Dr. YOUSSEF BARAKAT YOUSSEF**
- **Prof. Dr. MAHER ABBAS EL-SOCKARY**

**Approved**

**Head of Chemistry Dept.**



## DEDICATION

*To My Dearest Husband Who Encouraged  
and  
Assisted me Strongly in Life, and  
Whose Love and Support  
Enabled me to Work Hard*

## ACKNOWLEDGEMENT

The author wishes to thank Professor Dr. **M. Farouk Ezzat**, Head of Egyptian Petroleum Research Institute, for his valuable guidance, helpful, advice and encouragement of this kind scientist .

The author wishes also to thank Professor Dr. **Nadia Abd-El-Hakim Youssef**, Professor of Physical Chemistry, Faculty of women, Ain Shams University, for her many valuable suggestions and stimulating discussions throughout this study .

The author wishes also to offer special word of appreciation to Professor Dr. **Youssef Barakat**, Department of Process Design and Development, EPRI, for suggesting the problem and supervising this work, without his valuable teachings, this study would not be possible.

The author wishes also to thank Professor Dr. **Maher El-Sockary**, Department of Petroleum Applications, EPRI, for his useful advices and help .

The author wishes also to acknowledge Dr. **Tahany Shinoda Gendy**, Assistant Professor, Department of Process Design and Development, EPRI, for her unfailing help in the computational part which gave a special flavour to this study .

The author wishes also to express her deep gratitude and thanks to Dr. **Attia Ibrahim Mead**, Faculty of Education, Suez Canal University, for his guidance and sincere help in corrosion inhibition measurements and discussions .

Thanks are also to all the staff members of Petroleum Applications Department, EPRI, for their support .

## CONTENTS

	Page
AIM OF THE WORK	
SUMMARY . . . . .	i
I. THEORETICAL SECTION	
I.1. Introduction . . . . .	1
I.2. Characteristic Features and Uses of Commercially Available Cationic Surfactant . . . . .	3
I.2.1. Long-chain amines and their salts . . . . .	3
I.2.2. Diamines and polyamines and their salts . . . . .	4
I.2.3. Quaternary ammonium salts . . . . .	5
I.2.4. Amine oxides . . . . .	8
I.2.5. Quaternized polyoxyethylenated long-chain amines . . . . .	10
I.2.6. Polyoxyethylenated long-chain amines . . . . .	12
I.3. Micellization and Solubilization by Aqueous Cationic Micellar Solutions . . . . .	17
I.3.1. Thermodynamic aspects . . . . .	17
I.3.2. Micellar characteristics . . . . .	20
I.3.3. Solubilization by aqueous cationic micellar solutions. . . . .	22
I.4. Emulsification of Asphalt . . . . .	24
I.4.1. Asphalt emulsion ingredients . . . . .	24
I.5. Corrosion and Types of Corrosion Inhibitors . . . . .	30
I.5.1. Corrosion inhibitors . . . . .	30

	Page
I.5.2. Types of inhibitors . . . . .	31
I.5.3. Stability of organic compound and inhibition . . .	33
 II. EXPERIMENTAL SECTION	
II.1. Preparation of Ethoxylated Primary Amines . . . . .	37
II.2. Surface Tension Measurements . . . . .	41
II.2.1. Critical micelle concentration . . . . .	42
II.3. Solubilization Experiments . . . . .	43
II.3.1. Middle phase microemulsion . . . . .	43
II.3.2. Solubilization parameter . . . . .	45
II.4. Emulsification Experiments . . . . .	48
II.4.1. Preparation of asphalt emulsion . . . . .	48
II.4.2. Testing of the obtained emulsion . . . . .	50
II.5. Corrosion Inhibition Experiments . . . . .	51
II.5.1. Corrosion working procedures . . . . .	51
II.5.2. Calculation of corrosion current (Tafel line extrapolation) . . . . .	53
II.5.3. Calculation of the degree of surface coverage using Langmuir isotherm . . . . .	54
II.5.4. Analysis of steel sample . . . . .	55
 III. RESULTS AND DISCUSSION . . . . .	
III.1. Micelle Formation and CMC . . . . .	58
III.2. Thermodynamic Parameters of Micellization . . . . .	88

	Page
III.2.1. Standard free energy change upon micelle formation . . . . .	88
III.2.2. Standard enthalpy change upon micelle formation . . . . .	90
III.2.3. Standard entropy change upon micelle formation . . . . .	92
III.3. Surface Properties of Ethoxylated Amines . . . . .	98
III.3.1. Surface excess and area per molecule . . . . .	98
III.3.2. Effectiveness and efficiency of surface tension reduction . . . . .	102
III.4. Thermodynamic Parameters of Adsorption . . . . .	112
III.5. Equations Relating CMC and % EO . . . . .	117
III.6. Solubilization of Hydrocarbons by Aqueous Cationic Micellar Solutions . . . . .	128
III.6.1. Phase boundaries . . . . .	128
III.6.2. Solubilization parameter . . . . .	129
III.7. Asphalt Emulsion Formulations Using Ethoxylated Amines. . . . .	141
III.7.1. Asphalt emulsion formulations using ethoxylated amines emulsifiers . . . . .	141
III.7.2. Asphalt emulsion formulations using ethoxylated amines co-emulsifiers . . . . .	143
III.8. Investigation of The Electrochemical Behaviour of steel in aqueous Solution of Hydrochloric Acid . . . .	152.



	Page
III.8.1. Potentiodynamic current-potential curve of steel in hydrochloric acid . . . . .	152
III.8.2. Corrosion current density, $i_c$ . . . . .	153
III.9. Corrosion-Inhibition of Steel in Aqueous Solutions of Hydrochloric Acid . . . . .	155
III.9.1. Effect of inhibitors on the corrosion of steel in sulphuric acid . . . . .	157
IV. CONCLUSIONS . . . . .	167
V. APPENDICES . . . . .	171
VI. REFERENCES . . . . .	191
VII. ARABIC SUMMARY	

## AIM OF THE WORK

Interest in surfactant applications has intensified in the last decades . The intensity of this interest will be sustained in the future for a simple reason that novel applications of surfactants have no end .

Some different areas of applications for ionic surfactants have been covered in a number of research programs and projects which have been carried out in the Egyptian Petroleum Research Institute (EPRI) . Some of these applications are currently of widespread industrial importance such as : asphalt emulsions for paving and construction, micellar flooding for the enhancement of oil recovery, ore flotation and in particular, the surface phenomena involved in this process for de-ashing and upgrading of petroleum coke . In addition, there are some other areas of application which offer possibilities for the future such as micellar catalysis and hydrocarbon-type separation.

This study emphasizes the surface properties and thermodynamic parameters of ethoxylated primary amines focusing on structure-performance correlation through a computational approach . As such, we feel it should be of interest to those engaged in both pure academic research and industrial application and development . After considering these topics from a physical chemistry perspective, the investigated compounds are evaluated as corrosion inhibitors, hydrocarbon solubilizers and asphalt emulsifiers .

## SUMMARY

## SUMMARY

This study is divided into two main sections . The first deals with the preparation of ethoxylated decyl-, dodecyl-, hexadecyl-, and octadecyl primary amines having different polyoxyethylene (POE) chain lengths . The phase behaviour of these compounds, at the aqueous solution-air interface, is investigated . The second section deals with the applications of these surface-active compounds as emulsifiers for some hydrocarbon-types and asphalt (i.e., behaviour at aqueous solution-hydrocarbon interface), and as corrosion inhibitors for API 5LX Grade X60 steel, widely used for petroleum industry (i.e., behaviour at aqueous solution-steel interface) .

**The first section** starts with the determination of the critical micelle concentration (cmc) of the prepared compounds from the surface tension ( $\gamma$ ) - log concentration isotherms at 25°, 35°, 45° and 55 °C using the least-squares regression analysis, then proceeds to the thermodynamic parameters of micellization ( $\Delta G_{mic}^o$ ,  $\Delta H_{mic}^o$  and  $\Delta S_{mic}^o$ ) and adsorption ( $\Delta G_{ad}^o$ ,  $\Delta H_{ad}^o$  and  $\Delta S_{ad}^o$ ) . Surface properties such as surface tension at cmc ( $\gamma_{cmc}$ ), the maximum surface excess concentration ( $\Gamma_{max}$ ), the area per molecule at the aqueous-air interface ( $A_{min}$ ), the effectiveness ( $\Pi_{cmc}$ ) and the efficiency (pC<sub>20</sub>) of surface tension reduction are among the discussed values . Also, the relation between the cmc and the degree of ethoxylation (% EO) is considered .

Based on data obtained from this section, the study reveals that the cmc values of the investigated compounds decrease with increasing temperature (T) and/or hydrophobic alkyl group chain length (R) whereas, an increase in cmc values is noticed with increasing the hydrophilic polyoxyethylene (POE) chain length. The effects of T, R and POE chain length, on the main thermodynamic quantities relevant to micellization and adsorption, show that both  $\Delta G_{mic}^{\circ}$  and  $\Delta G_{ad}^{\circ}$  become more negative with increasing T and/or R and become slightly less negative with increasing POE chain length.  $\Delta H_{mic}^{\circ}$  and  $\Delta H_{ad}^{\circ}$  decrease with increasing R but the reverse is observed with increasing POE chain length.  $\Delta S_{mic}^{\circ}$  and  $\Delta S_{ad}^{\circ}$  values are all positive and increase with increasing POE chain length, whereas, a less pronounced undefined effect is exhibited by increasing R chain length.

Surface properties data reveal that  $\Gamma_{max}$  values decrease with increasing T and/or POE chain length but an insignificant effect is observed by increasing the length of R.  $A_{min}$  value increases with increasing T and is inversely proportional to  $\Gamma_{max}$ . The achieved results also reveal that the investigated compounds have  $\Pi_{cmc}$  and  $pC_{20}$  values in the vicinity of ethoxylated nonionics with comparable R and degree of ethoxylation.

The relationship between the cmc and % EO is found to be represented satisfactorily by the linearized equation :  
 $\ln \text{ cmc} = a + b (\% \text{ EO})$ . The constants (a) and (b) are determined at 25, 35, 45 and 55 °C using the least-squares regression analysis.

ethoxylated octadecylamines do not obey this logarithmic equation but is best represented by a linear one .

The **second section** of this study deals with the applications of the investigated compounds as emulsifiers (Part I) and as corrosion inhibitors (Part II) .

In part I of this section, the solubilization parameters of oil and/or water are measured . The obtained data reveal that for each oil phase, the solubilization parameter increases with the molecular weight of surfactant . Also, for a given molecular weight surfactant, the lower oil phase carbon number (OPCN), the higher the solubilization parameter . The solubilization parameter is generally found to be related to the interfacial tension between the aqueous surfactant solution and the oil phase . The lower the interfacial tension, the higher the solubilization parameter .

Data achieved from asphalt emulsion experiments show that ethoxylated amines are fairly good emulsifiers for asphalt emulsion formulations in which asphalt content does not exceed 30 % by wt. Only ethoxylated octadecylamines are successfully employed to stabilize 40 % asphalt emulsions . When the investigated ethoxylates are employed as co-emulsifiers in 60 % asphalt emulsions, stabilized with tallow diamine hydrochloride, the viscosity and stability of these emulsions are found to increase with increasing the degree of ethoxylation (% EO) of co-emulsifier . Results of this type clearly show that

ethoxylated amines are useful ingredients in the formulation of some paving asphalt emulsions having a controllable viscosity .

In Part II, the possibility of using some ethoxylated primary amines (e.g. dodecylamine) having different degrees of ethoxylation (% EO) as corrosion inhibitors for API 5LX Grade X60 steel in 0.5 M aqueous HCl solution, is investigated at 30 °C using potentiostatic techniques . The increase in the inhibitor concentration gives rise to the following effects :

1. Ethoxylated primary amines act as mixed type inhibitors and exhibit Tafel-type behaviour . Also, corrosion inhibition has a pronounced influence on cathodic polarization .
2. The corrosion potential ( $E_{corr}$ ) of the steel electrode is not affected by inhibitor concentration . On the contrary, the corrosion current density ( $i_c$ ) is strongly reduced by the addition of these compounds and the inhibitor efficiency increase .

In 0.5 M  $H_2SO_4$ , the obtained results reveal that the investigated ethoxylated amines are less effective corrosion inhibitors if compared with their performance in 0.5 M HCl aqueous solution .