A STUDY ON SOME APPLICATIONS FOR SOME SURFACE-ACTIVE AGENTS

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A STUDY ON SOME APPLICATIONS FOR SOME SURFACE-ACTIVE AGENTS

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بسم الله الرحمن الرحيم

DEDICATION

To My Dearest Husband Who Encouraged

and

Assisted me Strongly in Life, and

Whose Love and Support

Enabled me to Work Hard

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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

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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 (γ) - log concentration isotherms at 25^o, 35^o, 45^o and 55 ^{o}C using the least-squares regression analysis, then proceeds to the thermodynamic parameters of micellization (ΔG^o_{mic}, ΔH^o_{mic} and ΔS^o_{mic}) and adsorption (ΔG^o_{ad}, ΔH^o_{ad} and ΔS^o_{ad}) . Surface properties such as surface tension at cmc (γ_{cmc}), the maximum surface excess concentration (Γ_{max}), the area per molecule at the aqueous-air interface (A_{min}), the effectiveness (Π_{cmc}) and the efficiency (pC_{20}) 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 ΔG^o_{mic} and ΔG^o_{ad} become more negative with increasing T and/or R and become slightly less negative with increasing POE chain length . ΔH^o_{mic} and ΔH^o_{ad} decrease with increasing R but the reverse is observed with increasing POE chain length . ΔS^o_{mic} and ΔS^o_{ad} 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 Γ_{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 Γ_{max} . The achieved results also reveal that the investigated compounds have Π_{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 cmc = a + b (% EO) . The constants (a) and (b) are determined at 25, 35, 45 and 55 ^{o}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 controlable 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 .