RESEARCH ARTICLE

SOLUBILIZATION OF DI-AND POLY-AROMATICS USING NONIONIC SURFACTANTS

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ABSTRACT

The effect of three selected concentrations of the nonionic surfactant, polyoxyethylenated (23) monolaurate (I) and polyoxyethylenated (23) monostearate (II) on an artificial oil spill was studied. Surface tension measurements were used to detect the critical micelle concentration (CMC). The hydrophobic-Lypophilic balance, HLB, was calculated and the wetting Power was determined for the prepared surfactants. Gas Chromatography (GC) was used to detect the most effective surfactant as a dispersing agent; also, the pristine/phytane ratio was determined before and after treatment. The di- and poly-aromatic compounds were detected at 228 nm and 256 nm, respectively using the Ultra Violet technique (UV). The obtained results pointed out that the nonionic surfactant, II, can successfully be used as a dispersing agent especially at and above its critical micelle concentrations (CMC) with efficiency more than surfactant I, which is less effective at these concentrations but it shows a good result at low concentration range (i.e. below the CMC).

INTRODUCTION

Marine oil spills have become more common as offshore oil production and transport increased over the last few decades [Li *et al*., 2007; Anderson and LaBelle 2000]. The volume of crude oil being spilled into the environment has increased significantly especially now where that oil seems to have taken the center stage as the major source of energy to mankind. Spilled oil on the surface of water bodies limits gaseous exchange, entangles, and kills surface organisms, and coats the gills of fish [Otitoloju 2005]. Once the oil spilled into the sea, it suffers some natural processes like spreading, evaporation, and dissolution. Also, wind and waves influence the rate of spill spreading. All these factors lead to the spread of the oil spilled in the sea water and the formation of water-in-oil emulsion and/or dispersion which will pollute the marine environment and cause damage for the aquatic organisms. The first priority in any spill is to stop the source of leakage and the second is to contain the spill so that further environment damage does not occur. For this reason, most researches were designed to study the possibility of cleaning-up the oil in marine water [Shalaby and El-Shamy 2006]. It is generally accepted that no single technique will be capable of dealing with every oil spill. The spillage of crude oil into the environment and its far-reaching negative effects on the environment demands the development of various control strategies such as containment and recovery using booms [Wong and Stewart 2003], skimmers or pumps [Lambton 2002], sorbents, burning [Garo *et al*., 2004], and dispersants [Anderson *et al*., 2009]. The volume of oil spilled, the sensitivity of the receiving environment, the topography of the area, etc. will always dictate the type of control strategies deployed. Dispersants are usually introduced when there is need to urgently eliminate the floating mass of the oil slick, especially when the spillage is close to shorelines [Otitoloju 2005]. Dispersants are specific type of surfactants. Their molecules possess amphiphilic characters as they consist of hydrophilic moieties together with hydrophobic moieties. The use of dispersants to remedy and site is being examined in research laboratories [Mourrel and Schechter 1998]. Dispersants alter the

balance between natural dispersion and emulsification, pushing the balance strongly towards dispersion and away from emulsification. The formation of droplets increases the exposure of the oil to bacteria and oxygen, favoring biodegradation. However, the distribution of oil into the water column is increased. This study is designed to examine how the type of the surfactant head can affect its performance as dispersing agents for oil spill. To achieve this goal, the two surfactants I and II were used. These surfactants have similar ethylene oxide units and different hydrophobic chain.

EXPERAIMENTAL

Materials

Ethoxylated nonionic surfactants were prepared in the laboratory according to the method recorded elsewhere [Wrigley *et al*., 1957; El-Feky *et al*., 2009]. Oil polluted sea water sample was prepared in lab by the addition of crude oil that obtained from east desert to unpolluted sea water. Different concentrations of the tested surfactants were added to the oil polluted sea water and shake well for 6 h. After settled, the sample was poured in a separating funnel to separate the surface oil layer from the water layer [El-Shamy 2003].

Measurements

Surface tension

The surface tension of the tested surfactant samples were measured using Krüss Tensiometer K100, Krüss GmbH at room temperature.

Sinking time

The sinking time (wetting power) of the surface active agents under investigation was determined by measuring the sinking time in second of gray cotton skein in the surfactant solution using Daves and Clarkson method [Lissant 1974].

Gas Chromatography

The gas chromatography (GC) is selected as a good tool to detect the intensity of pollution before and after treatment with dispersant and to

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clarify the efficiency of each dispersant at the different concentrations under investigation. The gas chromatograms of the crude surface samples before and after treatment with surfactants were recorded on GC-17A Gas chromatograph, Shimadzu-(Japan) with methyl sillicon column. The column temperature was 70 ^{o}C (for 2 min.) and increased 7 ^{o}C/min until it reached 270 ^{o}C (for 10 min.). The detector and injector temperatures were 300 ^{o}C.

Ultra Violet spectroscopy

The Ultra Violet (UV) absorption for the subsurface water sample using Unicam UV2-100 UV/Visible spectrometer is used to detect the solubilization of di- and poly-aromatic compounds due to the presence of surfactant at wave length 228 nm and 256 nm, respectively.

RESULTS AND DISCUSION

Chemical Structure

Elemental Analysis

The carbon and hydrogen content of the used surfactant has been determined using CHN Elemental Analyzer Elementer Vario – EL (Germany). The matching between the measured and the theoretical percentage indicates the purity of the compound to be used as show in Table 1.

Table 1. Elemental analyses for nonionic surfactant (I)

Sample	Element			
	%C		%H	
	Found	Calculated	Found	Calculated
I	57.9	58.0	9.7	9.6
II	66.9	67.0	10.6	10.6

FTIR

The chemical structure of the prepared ethoxylated nonionic surfactants was confirmed by the FTIR which are shown the following absorption bands at 2886.92 cm^{-1}(CH$_2$str.), 1468.53 cm^{-1} (CH$_2$ bend.), 1111.76 cm^{-1} (C-O str.) and 1731.76 cm^{-1} (C=O). The FTIR spectra confirmed the expected function groups in the synthesized ethoxylated surfactants (Fig. 1 and 2).

Critical Micelle Concentration

The critical micelle concentrations (CMC) of the investigated surfactants were determined from the intercept point of the two linear portions given by the semi logarithmic plot of surface tension, γ (mNm^{-1}) versus log concentration, log C (mol dm^{-3}). A break is observed where the surface tension doesn't change further with concentration; this break represents the critical micelle concentration as observed in Figures (3 and 4) for the tested nonionic and anionic surfactants, respectively. The cmc values of the used surfactants are 2.51 x 10^{-4} mol dm^{-3} for (II) and 2.31 x 10^{-4} mol dm^{-3} for (I). It is clear from the data of CMC that it decrease with increasing the hydrophobic chain which is agreed with many authors [El-Feky *et al*., 2010].

Hydrophilic-Lipopholic Balance (HLB)

The HLB number of a surfactant is one of the most widely used indicators of its suitability for a given application. It is a measure of a surfactant partitioning tendency between oil and water and it calculated for an ethoxylated surfactant using Griffin's equation [El-Shamy *et al.*, 2011]:
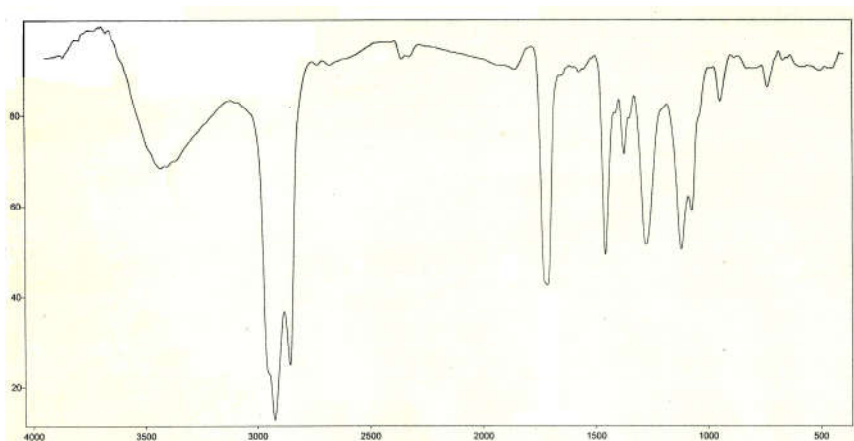
$$HLB = \frac{mass\,\%\,EO}{5}$$
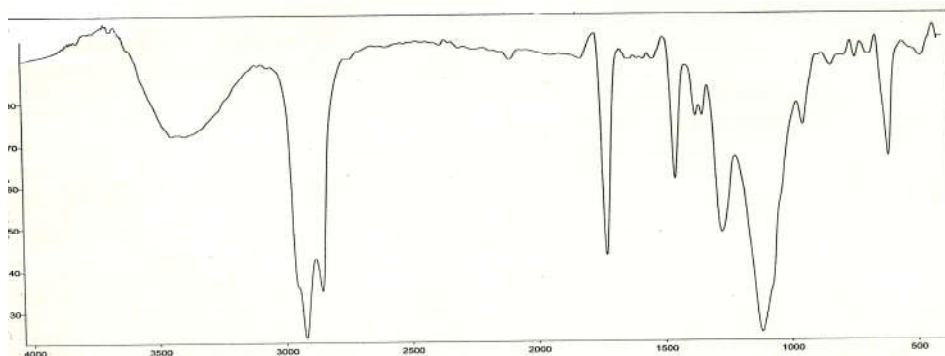

Fig. 1. FTIR spectra for surfactant I.

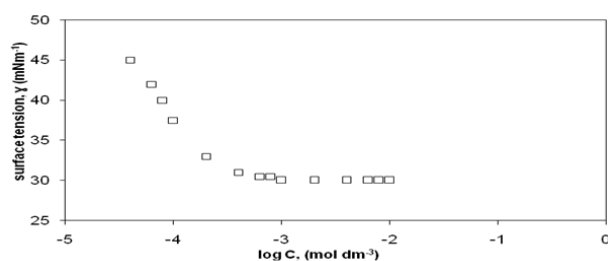**Fig. 2. FTIR spectra for surfactant II.**

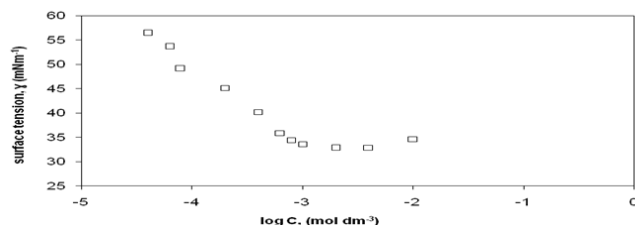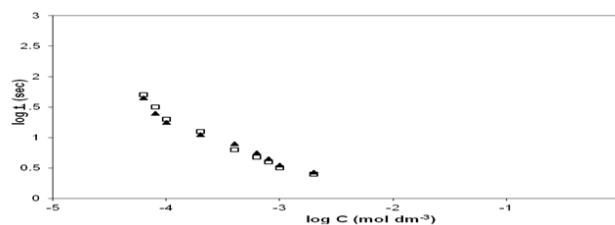**Fig. 3. Variation of surface tension with log concentration for I.**

Fig. 4. Variation of surface tension with log concentration for II.

Where, mass % EO is the percentage of EO in the surfactant on the mass scale. From the calculated values and according to the HLB scales [El-Shamy 2003], it was found that the two surfactants can be considered not only as dispersing agents but also as good solubilizer (HLB = 16.6), in addition, both of them are considered as strong wetting agents. The HLB data revealed the good suitability of the selected surfactants in this application.

Sinking time

The sinking time logarithm were plotted versus log concentration. Fig. 5 declined that the logarithm of the sinking time is a linear function of the log of the bulk phase concentration and decreased sharply as the surfactant concentration increases. This means that the tested surfactants possess wetting power confirmed the HLB results.

Variation of log sinking time with log surfactant concentration: I ($\square$) and II ($\blacktriangle$)

Gas Chromatography measurements (GC)

The GC profile of the untreated polluted sea water in Fig. 6 shows that the chromatogram has a homologous series of n-alkanes distributed with regularly spaced of gradually changed size. Also, the two majored acyclic isoprenoids pristane (C_{17}) and phytane (C_{18}) are present. All arranged over a large unresolved complex mixture (UCM), which is the general feature of the used petroleum crude oil [El-Shamy 2003]. The GC profile of the original sample (i.e. untreated oil polluted sea water) shows the absence of low molecular weight hydrocarbons ranged from (C_1-C_{10}) where they were easily
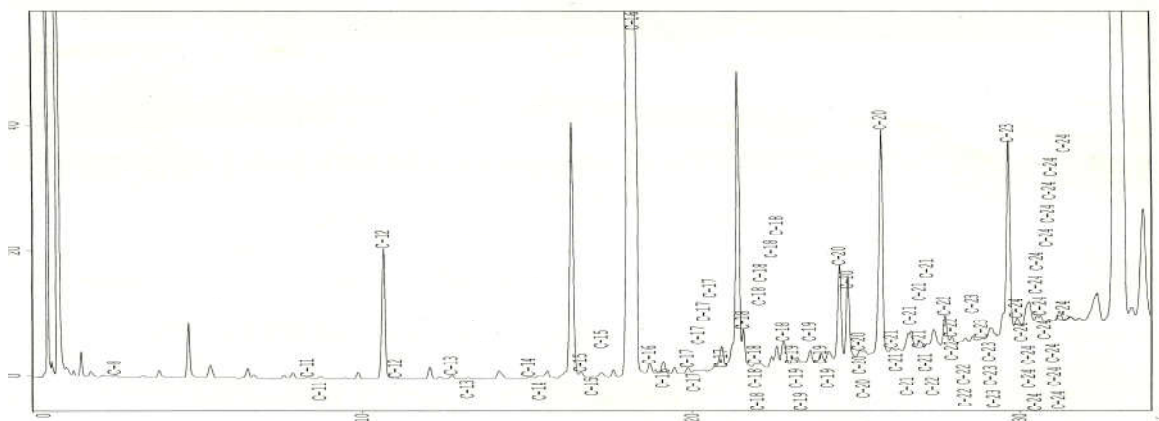

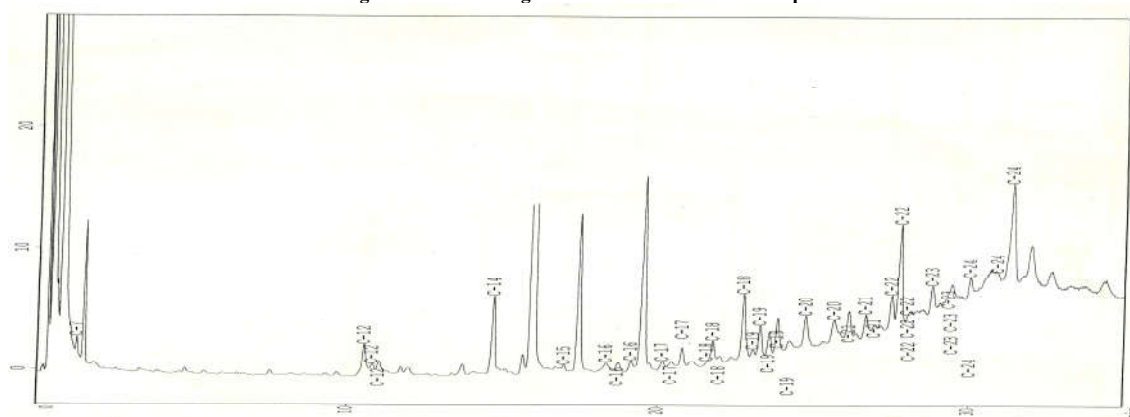**Fig.6. Gas Chromatogram for untreated surface sample**

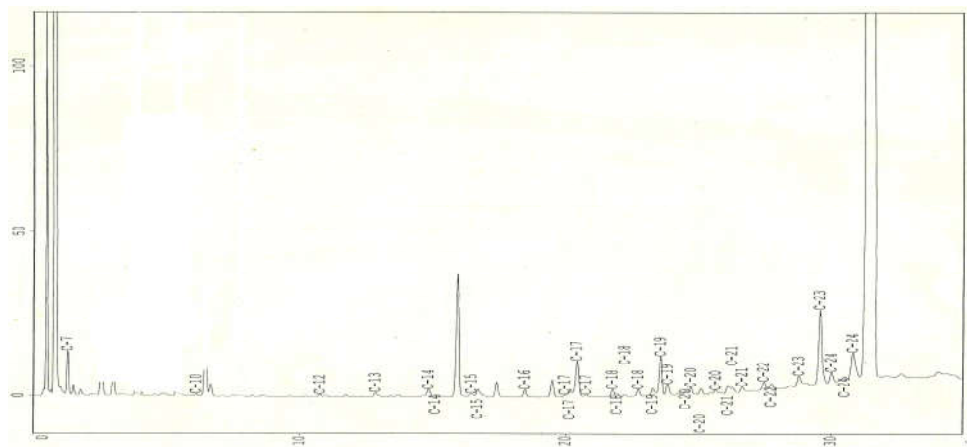**Fig.7. Gas Chromatogram for treated surface sample with II before CMC**

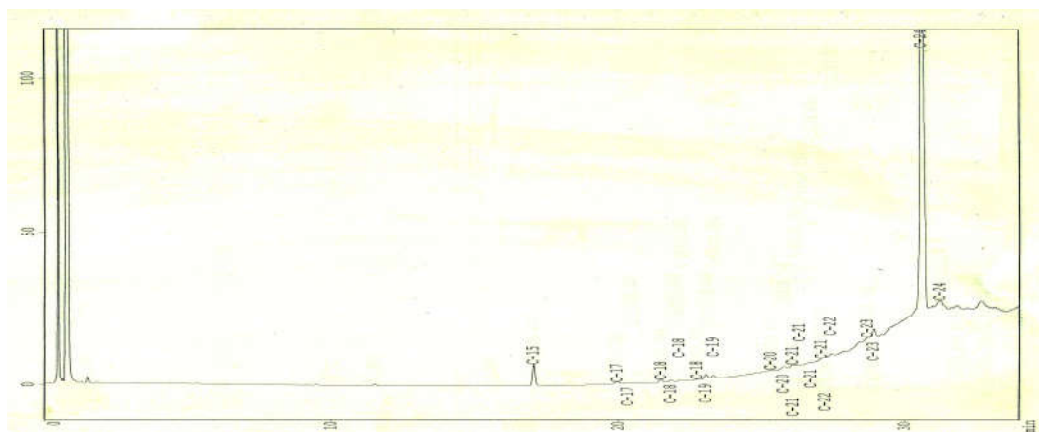**Fig.8. Gas Chromatogram for treated surface sample with II at CMC**

Fig.9. Gas Chromatogram for treated surface sample with II after CMC

vaporized. The GC-profile of the polluted surface that was treated with different concentrations of the tested nonionic surfactant II is defined and given in Figure (7, 8 and 9). At low surfactant concentration (i.e. below the cmc), there is no great effect observed (Figure 7) while a good dispersion efficiency is observed with concentrations at and above the critical micelle concentration [Figure 8 and 9]. This behavior reflects the solubilization of the oil droplets into the hydrophobic core of the micelle of this surfactant which contain long hydrocarbon chain. This result is in line with the feature discussed before [Deshpande *et al*., 2000] as the author decided that the surfactant monomers aggregate to form micelles with the hydrophobic portion of the molecules in the center and the hydrophilic portions at the micelle. The hydrophilic exterior of the micelles makes them highly stable in water while the contaminants partitioning into the hydrophobic micelle interior increases their apparent solubilization. Surfactant I has similar trend as surfactant II but with less efficiency (GC-Profile not include). Because the aromatic components are polar in nature, it would be expected that they favor to solubilize in the palisade region of the micelles. This behavior gives the reason for the high treating of polluted water by investigated surfactants at and above its critical micelle concentration [Shalaby and El-Shamy 2006]. The two isoprenoids, pristine and phytane (C_{17} and C_{18}, ratio of the respectively) and their ratio was calculated before and after the addition of surfactants and the obtained data are tabulated in Table (2). The decrease in the value of these ratios with the increase in the surfactant concentrations confirms the effect of the used surfactant on the resistant isoprenoid compounds [Shimy *et al*., 1995]. A different feature than in cse of La(EO)$_{14}$ has been shown in Figure (5 a,b,c) for the GC profile of the surface oil pollutant treated with the anionic

surfactant SDS at concentrations: below, at, and higher than cmc, respectively. At low concentration, i.e. below cmc, the chromatogram shows markedly decrease in the concentration of all the hydrocarbons series compared with the GC chromatogram before treatment as presented in Figure (5a). The efficiency of SDS is greater not only on the lower hydrocarbons but its effect reaches also the higher hydrocarbon series. Despite of the resistance of isopernoides pristane and phytane to different weathering conditions [Pastor *et al*., 2001], the chromatogram declares that there is a significant decrease in their concentrations and hence their ratio as represented in Table 2.

Table 2. The pristine / phytane ratio for surface oil sample with and without surfactants

Surfactant		Pristane/phytane
----		0.916
I	before CMC	0.625
	at CMC	0.667
	after CMC	0.659
II	before CMC	0.689
	at CMC	0.556
	after CMC	0.504

The pristane / phytane ratio with both surfactant concentrations at and above the cmc are slightly affected, which confirmed the efficiency of them as dispersing agent for oil polluted sea water. Ultra violet spectroscopy is a sensitive tool for qualitative determination of aromatic hydrocarbons and various heterocyclic compounds [Shimy *et al*., 1995]. Saturated hydrocarbons such as paraffins do not respond

to this technique. The UV absorption spectra is used to detect the solubilization of di- (at 228 nm) and poly-aromatics (at 256 nm) due to the presence of the tested surfactants. The spectrogram of the water sample that was treated by each surfactants especially at low concentration shows a peak at 228 nm while another with higher surfactant concentration (at cmc) another peak at 256 nm appears. This indicates that surfactant under investigation possess a great efficiency to solubilize di-aromatic compounds of the oil surface presents in water column and hence great facility for the biodegradation of these compounds. Above the cmc, the efficiency of the solubilization of both di- and poly- aromatics increases (Figure not include). The results of UV with those obtained from GC are matched and confirm each other.

Conclusion

- Surface tension measurements were used to determine the CMC for the investigated surfactants.
- The sinking time measurements were declared the strong wetting power of the investigated surfactants.
- HLB values were declared that the investigated surfactants considered as solubilizig agents.
- Surfactant II exhibits higher dispersion and solubilization for both di- and poly- aromatics as confirmed by both GC and UV comparing with surfactant I.

Acknowledgement

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