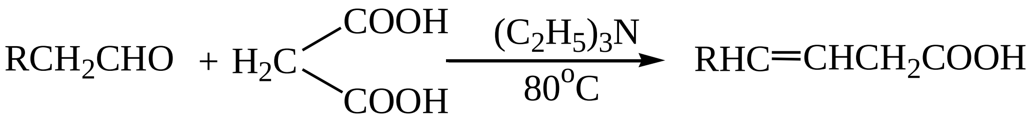
# Results and Discussion

## *Preparation of 3-alkenoic acid:*

Long chain 3-alkenoic acids are useful intermediates for the synthesis of variety of organic compounds. The reaction of malonic acid with carbonyl compounds (Knoevenagel condensation) is an important synthetic route to valuable unsaturated acids and α-β-unsaturated acids in high yields. The 3-alkenoic acid was prepared from the reaction of aldehydes with malonic acid in the presence of triethylamine in molar ratio of 1:1;1.5, respectively, as the following equation:



$$RCH_2CHO + H_2C(COOH)_2 \xrightarrow[80^oC]{(C_2H_5)_3N} RHC{=}CHCH_2COOH$$

Where R = $CH_3(CH_2)_7$ and $CH_3(CH_2)_9$.

The acid value of the products were determined and were found to be 225, 197 for 3-dodecenoic and 3-tetradecenoic acid respectively.

The structure of the prepared 3-alkenoic acids was confirmed *via* their IR and $^1$H-NMR spectra. The IR spectrum of 3-alkenoic acids show the following bands in cm$^{-1}$, broad band at 3442 cm$^{-1}$ corresponding to ν –OH band, 2989 cm$^{-1}$ for –CH- aliphatic for alkyl chain, 1691 cm$^{-1}$ corresponding to ν -CO of acid. (*cf.* fig.1).

$^1$H-NMR spectra of 3-alkenoic acid revealed at δ = 0.89 (t, 3H, terminal $CH_3$), 1.21-1.43 ( m, 12H, of alkyl chain), 2.00 (q, 2H, -$\underline{CH_2}$-CH=CH- ), 3.05 (d, 2H, -CH=CH-$\underline{CH_2}$-C=O), 5.45-5.64 (m, 2H, -$\underline{CH}$=$\underline{CH}$-), 9.80 (s, 1H, COO$\underline{H}$ ) see (figs. 35, 36).

# Part (I)

## Synthesis and surface properties of several nonionic–anionic surfactants derived from alkenoic acid and its derivatives :

An nonionic surfactants and nonionic-anionic surfactants were prepared from the alkenoic fatty acid (3-dodecenoic acid, 3- tetradecenoic acid and 9- octadecenoic acid), and the dihydroxy methyl ester of these fatty acids after hydroxylation of the double bond in each acid. The non-ionic surfatcatnt were prepared first by the propenoxylation of all prepared compounds followed by sulfation of these oxypropenoxylated compounds to give anionic-nonionic surfactants (Scheme 1).

### *I.a Fatty acids methyl esters :*

The conversion of unsaturated fatty acids ( 3-dodecenoic, 3-tetradecenoic and 9- octadecenoic acids) into methyl ester were achieved by conventional methods(6), The structure of the prepared methyl esters were confirmed by IR spectra. The IR spectrum for methyl 3-tetradodecenoate revealed characteristic band at 1743.5 $cm^{-1}$ corresponding to ν -CO of ester and showed also the disappearance of ν of –OH band. (*cf.* Fig. 2).

### *I.b Vicinal dihydroxy alkanoic acid methyl ester:*

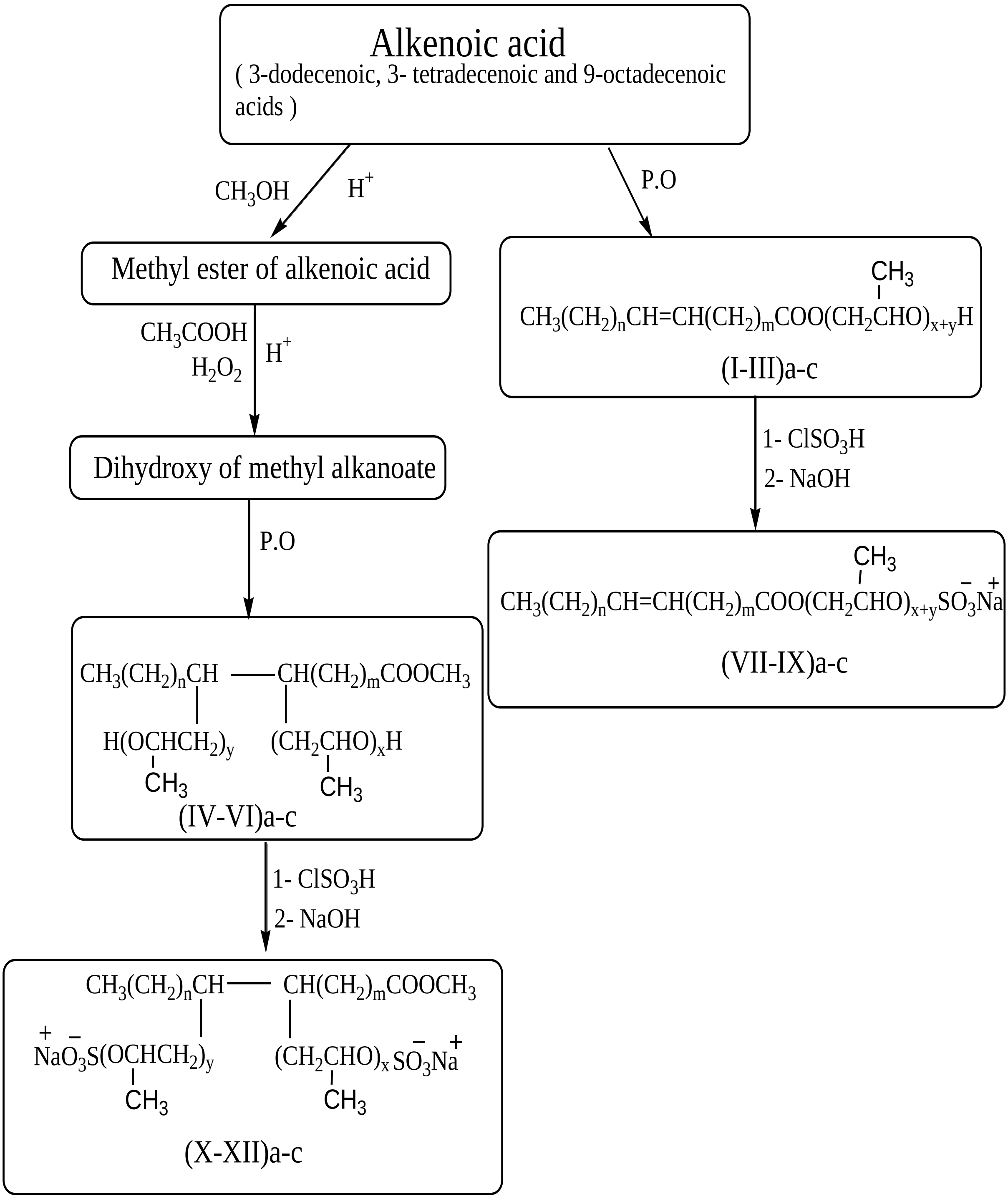
Refluxing alkenoic acid methyl ester with glacial acetic acid and hydrogen peroxide in the presence of sulfuric acid as catalyst, followed by hydrolysis with KOH in water-ethanol mixture afforded cis-dihydroxy alkanoate methyl ester.

The structure of cis-3, 4-dihydroxy tetradecanoate methyl ester was confirmed *via* their IR and $^1$H-NMR spectra. IR spectrum shows that, two characteristic bands at 1734 $cm^{-1}$ corresponding to ν -CO of ester and 3403 $cm^{-1}$ corresponding to ν –OH of diol (*cf.* Fig 3). The $^1$H-NMR spectrum gave characteristic signals, at δ = 0.81 (t, 3H, terminal $\underline{CH}_3$), 1.21-1.48 ( m, 18H, of alkyl chain), 2.22 (d, 2H, -$\underline{CH_2}$-CO ), 3.41 (m, 2H, -$\underline{CH}$(OH)-$\underline{CH}$(OH)), 3.84 (3H, -O$\underline{CH_3}$), 6.26 (s, 2H, -CH($\underline{OH}$)-CH($\underline{OH}$)) protons of diol which disappear by addition of $D_2O$ (*cf.* Fig 37, 38).

## *I.c Nonionic surfactants:*

Nonionic surfactants have a wide range of applications they are excellent emulsifiers, and used as chemical intermediates of anionic surfactants and also used in many industrial applications. They can be synthesized with a variety of head groups, such as sugar esters, alkanol amides and amine oxides. the most commonly studied nonionic surfactants are alkoxylated nonionic surfactant. They are prepared by the addition of different moles of ethylene oxide or propylene oxide.

The availability of propylene oxide at a relatively low price, coupled with its ease of reaction to form poly propylene glycols opens the way to an unlimited number of relatively base materials for the synthesis of non-ionic surfactants. In the present work the nonionic surfactants were prepared through the reaction of the prepared compounds with propylene oxide using KOH as catalyst. Alkenoic fatty acids (3-dodecenoic, 3-tetradodecenoic and 9-octadecenoic) and dihydroxy fatty acid methyl esters were oxypropenoxylated with different molar ratio (n = 5, 7 and 10 mole) of propylene oxide. To give oxypropenoxylated fatty acids ($I_{a-c}$- $III_{a-c}$), and oxypropenoxylated dihydroxy fatty acid methyl ester ($IV_{a-c}$-$VI_{a-c}$).



Where n = 7,9,7 , m= 1,1,7 and x+y = 5,7 and 10 mol P.O

Scheme 1

## *I.c.1 -Nonionic surfactants from alkenoic fatty acids:*

The oxypropenoxylated alkenoic fatty acids (3-dodecenoic, 3-tetradecenoic and 9- octadecenoic) prepared by addition of propylene oxide with different molar ratio (n = 5, 7 and 10 mole), to give oxypropenoxylated fatty acids ($I_{a-c}$- $III_{a-c}$).

The structures of the prepared nonionic surfactants were confirmed by using IR and $^1$H-NMR spectra, The IR spectrum of oxypropenoxylated 3-dodecanoic acid (5,7,10 mole) (Ia-c) (Fig. 4-6), all these figures showed characteristic bands of the ether linkage of polypropenoxy chain (ν C-O-C) at 1100-1120 cm$^{-1}$ and at 1735 cm$^{-1}$ characteristic for ν CO of ester. $^1$H-NMR spectra showed that, the characteristic protons of propenoxy group at δ = 3.31-3.50 ppm (*cf.* Fig 39).

## *Surface active properties:*

The surface active properties and related properties, including surface and interfacial tension, cloud point, wetting time, foam height and emulsion stability were investigated to evaluate the possible application of these products in different industrial fields.

### 1- Surface and Interfacial tensions :

The surface and interfacial tension of the prepared oxypropenoxylated fatty acids ($I_{a-c}$- $III_{a-c}$) are given in (table 1). It showed that, the values of surface and interfacial tension of the oxypropenoxylated fatty acids increases as the mass of hydrophilic groups (propylene oxide units) increase within the range under study. It is also indicated that the oxypropenoxylated 3-dodecenoic and 3- tetradodecenoic acids ($I_{a-c}$- $II_{a-c}$) have lower values of surface and interfacial tension than oxypropenoxylated oleic acid ($III_{a-c}$).

## 2- Cloud point:

The aqueous nonionic surfactants solutions at above certain temperature phase separation occur to form surfactant rich face (coacervate phase) and a surfactant dilute phase. The dilute phase is an aqueous solution containing surfactant monomers or micelles(195).Such system is called a cloud point system and the phase separation temperature is called a cloud point at which the turbidity occurs.

The cloud points of the prepared surfactants are shown in (table 1). It was found that; all the nonionic surfactants are soluble at room temperature and the cloud point of these compounds increase with increasing the number of propylene oxide units per hydrophobic molecule(23).

## 3- Wetting time :

Wetting agents a substance, which when added to a liquid, increase its spreading and penetrating power by lowering the surface tension. Nonionic surfactants are among the most powerful wetting agents available. The wetting properties of 1.0 % solutions in distilled water were measured. Table 1 showed that the wetting time increase as increasing the alkyl chain length. Also it found that the nonionic surfactants with low hydrophilic units content had a good wetting time(196).

## 4- Emulsifying properties :

The emulsifying efficiency of a surfactant was related to the polarity of the molecule or the relation between the contribution of the polar hydrophilic head and the nonpolar lipophilic tail. From the data recorded in (table 1) the emulsifying properties increased with decreasing the number of propylene oxide units into the molecule(23). Also the emulsifying properties increased with increasing the alkyl chain length of the fatty acid(197).

## 5- Foaming Power:

It was reported that; nonionic surfactants have low and unstable foam. The low foaming tendency of surfactant is recently considered as an important property in some applications such as dyeing industry. On the other hand the foam height of the prepared surfactants gave low foam and it slightly increase with increasing the propylene oxide unit per molecule.

## 6- Critical micelle concentration *(CMC)* :

Micelles only form above a characteristic concentration called the Critical Micelle Concentration *(CMC)*. Below the *CMC* surfactants exist as separate molecules (or monomers). The value of the *CMC* depends on the surfactant structure, especially the tail.

Figure 52 shows the variation in surface tension of aqueous solutions of compounds ($I_{a-c}$- $III_{a-c}$) versus, surfactant concentration, plotted as its logarithm to determine the break point indicates the *CMC*. The values of the *CMC* were collected in the table 1, indicate that an increase the propylene glycol units in the molecule reduce the *CMC*(198), Also the values of *CMC* decrease with increasing the number of carbon atoms in the hydrophobic group(98).

## 7- Biodegradability:

It is a natural process by which organic or carbon-containing material is decomposed by micro organisms. A biodegradable surfactant is broken down by bacteria. The result of the biodegradability as shown in table 5, reflected the fact that, it decreased with the increasing of the repeating units of propenoxy group as well as, the repeating alkyl groups in the hydrophobe unit(113).

## *I.c.2-Nonionic surfactants from dihydroxy fatty acids methyl ester:*

As we prepared nonionic surfactants from alkenoic fatty acids (3-dodecenoic, 3-tetradodecenoic and 9-octadecenoic) by oxypropenoxyltion, these fatty acids were converted to its methyl ester followed by hydroxylation of the double bond. The dihydroxy products were reacted with different moles (n) of propylene oxide (n = 5, 7 and 10) to afford oxypropenoxylated dihydroxy alkenoic fatty acids methyl ester ($IV_{a-c}$- $VI_{a-c}$) as nonionic surfactant.

The structures of the synthesized nonionic surfactants were confirmed via IR and $^1$H-NMR spectra, The IR spectrum of 3,4-(2-hydroxy-propoxy polypropenoxy) tetradecanoic acid methyl ester (Va-c) (Fig. 7- 9), all these figures showed characteristic bands of the ether linkage of polypropenoxy chain (ν C-O-C) at 1110-1180 $cm^{-1}$ and 1739-1742 $cm^{-1}$ characteristic for ν C=O of ester. $^1$H-NMR spectra showed that, the characteristic protons of propenoxy group at $\delta = 3.27-3.40$ ppm (*cf.* Fig 40).

## *Surface active properties:*

The surface and interfacial tension, cloud point, wetting time, foam height and emulsion stability were investigated and recorded in table 2.

### 1- Surface and Interfacial tensions:

The surface and interfacial tension of the prepared oxypropenoxylated dihydroxy fatty acids methyl esters ($IV_{a-c}$- $VI_{a-c}$) are given in (table 2). It is evident that the of surface and interfacial tension decrease as mass of hydrophilic groups decrease. Where, the oxypropenoxylated dihydroxy fatty acids methyl esters showed lower values than the corresponding fatty acids.

## 2- Cloud point:

The cloud points of the prepared surfactants are shown in (table 2). It showed that; all the cloud point values increase with increasing the number of propylene oxide units per hydrophobic molecule. When the data of cloud point in (table 2) compared with those of in (table 1) of oxypropenoxylated fatty acids, there is no big difference obtained.

## 3- Wetting time:

Wetting time of the synthesized surfactants were listed in (table 2), it reported that, the nonionic surfactants with lower mass and low propylene oxide content have a better wetting properties. And the oxypropenoxylated dihydroxy fatty acids methyl esters have better wetting properties than oxypropenoxylated fatty acids.

## 4- Emulsifying properties:

The emulsifying properties increased with decreasing the number of propylene oxide units and with increasing the alkyl chain length of the fatty acid. But the oxypropenoxylated dihydroxy fatty acids methyl esters were less than oxypropenoxylated fatty acids in the emulsifying properties (*cf*. table 2).

## 5- Foaming Power:

In general, the nonionic surfactants show low and unstable foam. The prepared surfactants gave low foam and it slightly increase with increasing the propylene oxide unit per molecule.

## 6- Critical micelle concentration *(CMC)*:

The data of the surface tension plotted against the concentration in logarithm to give the *CMC* values. Figure 53 shows the *CMC* values for the compounds ($IV_{a-c}$- $VI_{a-c}$). The values of the *CMC* were collected in the (table 2), indicate that an increase the propylene glycol units in the molecule reduce the *CMC*. When the data in (table 2) compared with those in (table 1), it showed that the CMC of the dihydroxy methyl ester surfactants are somewhat higher than that of the corresponding fatty acids surfactants.

## 7- Biodegradability:

The result showed that, the rate of biodegradability was decrease with increasing the molecular weight or alkyl chain length. This indicates that, the more bulky molecule gave lower biodegradability of the surfactant(199) as shown in (table 6).

## I.d- Anionic-nonionic surface active agents:

Nonionic surfactants of the polypropylene type, generally exhibit excellent surfactant properties. But they have been found to have two primary disadvantages, however, in that they are seldom good foam producers (an advantage in some applications such as automatic washing machines) and under some conditions give cloudy solutions, which may lead to phase separation.

The sulphated anionic surfactants, on the other hand, generally have good foaming properties, but their more common sodium salts rarely produce clear solutions except at low concentrations. To achieve clarity it is often necessary to use some cation other than sodium, which may increase costs or introduce other difficulties.

When the nonionic surfactants prepared, the resulting ether still has a terminal –OH group, which can subsequently be sulfated to give the ether sulphated compound. The nonionic surfactants which prepared from the propenoxylation of fatty acids and dihydroxy fatty acid methyl ester can then be sulfated with chlorosulfonic acid and neutralized with sodium hydroxide, to yield the anioni-nonionic surfactants product ($VII_{a-c}$-$XII_{a-c}$).

This class of surfactant has been extensively investigated because it has the potential to combine the advantages of both the anionic and nonionic surfactant types.

The structure of the sulphated nonionic surfactants compounds ($VII_b$ and $XI_b$) were confirmed *via* IR spectra (fig. 10, 11), it shows the disappearance of characteristic band at 3416 $cm^{-1}$ corresponding to $\nu$ –OH band where it converted to $-OSO_3$.

## *Surface activity and related properties:*

The surface activity and related properties of the prepared sulfated oxypropenoxylated fatty acids ($VII_{a-c}$-$IX_{a-c}$) and oxypropenoxylated dihydroxy fatty acids methyl ester ($X_{a-c}$-$XII_{a-c}$) are given in table (tables 3, 4). The sulfation of oxypropenoxylated nonionic surfactants improved the solubility of these compounds; also the surface properties of the sulphated products were evaluated. The result indicates that, the surface active properties of the new anionic surfactants are improved by increasing the hydrophilcity in the starting molecule.

### 1- Surface and Interfacial tensions:

The surface and interfacial tension of the prepared sulphated oxypropenoxylated compounds ($VII_{a-c}$- $XII_{a-c}$) are given in (tables 3, 4). It was found that the surface and interfacial tension slightly decrease as mass of hydrophobic groups increase(98), and also increase with increasing the propylene oxide units per molecule. Also it showed relatively lower values of surface tension than those in (table 1, 2).

The sulphated oxypropenoxylated fatty acids show higher values of surface tension than sulfated dihydroxy fatty acid methyl ester, while the surfactants derived from 9-octadecenoic acid have nearly the same values.

### 2- Kraft point:

The kraft points of the prepared surfactants are shown in (tables 3, 4). It showed that, all the kraft point values increase with increasing the hydrophobicity(111). While it decrease with increasing the number of propylene oxide units per hydrophobic molecule. When the data of kraft point in (table 3) compared with those in (table 4), there is a slightly difference showed, while the ($VII_{a-c}$- $IX_{a-c}$) compounds have higher kraft point than ($X_{a-c}$-$XII_{a-c}$) compounds.

## 3- Wetting time:

The ease with which the surface can be wetted by water as other liquids is an important property suitable for many applications. The wetting time of the synthesized surfactants which listed in (tables 3, 4), showed that, the wetting time of sulphated compounds have higher values than those of oxypropenoxylated nonionic surfactants. The increase of propylene oxide units in the molecule causes increasing of the wetting time.

## 4- Emulsifying properties:

The process of emulsification is the dispersion or suspension of fine particles of one liquid in another immiscible liquid. The data are in (tables 3, 4) showed that, the emulsifying properties increased with decreasing the number of propylene oxide units and with increasing the alkyl chain length of the fatty acid. But the oxypropenoxylated compounds ($I_{a-c}$- $VI_{a-c}$) showed comparatively higher values than that of sulphated compounds ($VII_{a-c}$- $XII_{a-c}$) and better emulsifying properties.

## 5- Foaming Power:

Foaming power is a mass of bubbles formed on liquids by agitation. From the data obtained in (tables 3, 4) it showed that, the efficiency of surfactant as a foamier increases with increase the alkyl chain length. In general, the foam height of anionic-nonionic surfactants ($VII_{a-c}$- $XII_{a-c}$) was higher than that of nonionic surfactants ($I_{a-c}$- $VI_{a-c}$). The presence of propylene oxide units incorporated with sulphated group in the same molecule decrease the foam height(200) while the foam height decrease with increasing the percent of propylene oxide units in the molecule.

## 6- Critical micelle concentration *(CMC)*:

Figures 54, 55 shows the variations in surface tension of aqueous solutions of compounds $VII_{a-c}$- $XII_{a-c}$ versus surfactant concentration, plotted as its logarithm, to determine the break point indicating the *CMC*. The *CMC* values, presented in (Tables 3, 4), indicate that an increase in the propylene glycol intermediate chain length tended to reduce the *CMC*(112). We compared the data of *CMC* of sulphated oxypropenoxylated fatty acids and sulphated oxypropenoxylated dihydroxy fatty acids methyl ester, it shows that sulphated oxypropenoxylated fatty acids have lower *CMC* values. The anionic-nonionic surfactants have higher *CMC* values than those of nonionic surfactants.

## 7- Biodegradability:

The data of biodegradability of anionic-nonionic surfactant listed in (Tables 7, 8) showed that, inside the same type of series compounds, the variation in the rate of degradation results from the difference in the number of carbon atoms in the molecule. This means that, the rate of biodegradion was decreasing with increasing the number of carbon atoms in the alkyl chain. It also introduce that the anionic-nonionic surfactants are more biodegradable than nonionic surfactants.

Table (1): Surface properties of oxypropenoxylated fatty acids:

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-3}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ia** | $C_{12}$ | 5 | 42 | 11.5 | 43 | 60 | 52 | 15 | 0.95 | 43 |
| **Ib** | $C_{12}$ | 7 | 43 | 12 | 53 | 65 | 53 | 25 | 0.80 | 44 |
| **Ic** | $C_{12}$ | 10 | 44.5 | 14 | 56 | 75 | 40 | 35 | 0.65 | 46.5 |
| **IIa** | $C_{14}$ | 5 | 42 | 12 | 40 | 75 | 70 | 10 | 0.85 | 43 |
| **IIb** | $C_{14}$ | 7 | 42.5 | 12.5 | 44 | 73 | 61 | 20 | 0.60 | 45 |
| **IIc** | $C_{14}$ | 10 | 44 | 13 | 47 | 81 | 58 | 25 | 0.45 | 46 |
| **IIIa** | $C_{18}$ | 5 | 45.5 | 14 | 38 | 90 | 78 | 35 | 0.20 | 46 |
| **IIIb** | $C_{18}$ | 7 | 46 | 15 | 42 | 95 | 72 | 50 | 0.15 | 47 |
| **IIIc** | $C_{18}$ | 10 | 48 | 15.5 | 45 | 112 | 66 | 55 | 0.08 | 49 |

n = number of propylene oxide units

Table (2): Surface properties of oxypropenoxylated dihydroxy fatty acids methyl ester:

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-3}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| IVa | $C_{12}$ | 5 | 39 | 11 | 48 | 40 | 40 | 30 | 2.5 | 40 |
| IVb | $C_{12}$ | 7 | 40.5 | 13 | 59 | 56 | 41 | 30 | 1.5 | 41.5 |
| IVc | $C_{12}$ | 10 | 41 | 13.5 | 60.5 | 67 | 37 | 40 | 0.90 | 42.5 |
| Va | $C_{14}$ | 5 | 39 | 11 | 44 | 60 | 54 | 50 | 1.4 | 40.5 |
| Vb | $C_{14}$ | 7 | 41 | 13.5 | 45 | 62 | 52 | 50 | 0.90 | 43 |
| Vc | $C_{14}$ | 10 | 42 | 14.5 | 46 | 69 | 47 | 55 | 0.85 | 44.5 |
| VIa | $C_{18}$ | 5 | 43 | 14 | 38 | 70 | 62 | 50 | 0.35 | 44 |
| VIb | $C_{18}$ | 7 | 43.5 | 15 | 45 | 75 | 59 | 60 | 0.20 | 47 |
| VIc | $C_{18}$ | 10 | 44 | 16 | 47 | 78 | 54 | 65 | 0.15 | 49 |

n = number of propylene oxide

Table (3): Surface properties of oxypropenoxylated fatty acids sulfates:

| **Compound No.** | **R** | **n** | **Surface tension (dyne/cm) 0.1 %** | **Interfacial tension (dyne/cm) 0.1 %** | **Kraft Point °C 1.0 %** | **Wetting time (Second) 1.0 %** | **Emulsion stability (min : Sec.) 1.0 %** | **Foam height (mm) 1.0 %** | CMC (M) **$10^{-3}$** | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| **VIIa** | **$C_{12}$** | **5** | **36** | **11** | **11** | **76** | **7 : 30** | **170** | **1.9** | **37** |
| **VIIb** | **$C_{12}$** | **7** | **38** | **12** | **10** | **79** | **6 : 55** | **160** | **1.5** | **39** |
| **VIIc** | **$C_{12}$** | **10** | **39** | **12.5** | **8** | **84** | **6 : 39** | **150** | **0.90** | **40** |
| **VIIIa** | **$C_{14}$** | **5** | **35** | **11** | **13** | **80** | **7 : 20** | **175** | **1.7** | **36** |
| **VIIIb** | **$C_{14}$** | **7** | **37** | **11** | **12** | **82** | **7 : 15** | **170** | **0.90** | **37** |
| **VIIIc** | **$C_{14}$** | **10** | **38** | **11.5** | **11** | **87** | **7 : 09** | **150** | **0.75** | **38.5** |
| **IXa** | **$C_{18}$** | **5** | **32** | **12** | **15** | **75** | **8 : 00** | **190** | **0.95** | **33** |
| **IXb** | **$C_{18}$** | **7** | **34** | **13** | **14** | **85** | **7 : 42** | **180** | **0.65** | **35** |
| **IXc** | **$C_{18}$** | **10** | **37** | **13.5** | **12** | **93** | **7 : 24** | **170** | **0.15** | **38.5** |

n = number of propylene oxide

Table (4): Surface properties of oxypropenoxylated dihydroxy fatty acids methyl ester sulfates:

| **Compound No.** | **R** | **n** | **Surface tension (dyne/cm) 0.1 %** | **Interfacial tension (dyne/cm) 0.1 %** | **Kraft Point $^{o}C$ 1.0 %** | **Wetting time (Second) 1.0 %** | **Emulsion stability (min : Sec.) 1.0 %** | **Foam height (mm) 1.0 %** | CMC (M) **$10^{-3}$** | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Xa** | **$C_{12}$** | **5** | **33.5** | **12** | **9** | **84** | **5 : 24** | **190** | **5.5** | **34** |
| **Xb** | **$C_{12}$** | **7** | **38** | **13** | **8** | **81** | **5 : 11** | **175** | **4.5** | **39** |
| **Xc** | **$C_{12}$** | **10** | **38.5** | **13.5** | **7** | **97** | **5 : 05** | **160** | **3.0** | **40** |
| **XIa** | **$C_{14}$** | **5** | **33** | **11** | **10** | **89** | **5 : 20** | **190** | **3.1** | **34** |
| **XIb** | **$C_{14}$** | **7** | **34.5** | **12** | **8** | **85** | **5 : 25** | **200** | **2.5** | **36** |
| **XIc** | **$C_{14}$** | **10** | **36** | **12.5** | **8** | **75** | **5 : 19** | **195** | **1.9** | **38** |
| **XIIa** | **$C_{18}$** | **5** | **32** | **10.5** | **13** | **93** | **5 : 55** | **210** | **1.7** | **31.5** |
| **XIIb** | **$C_{18}$** | **7** | **34** | **11** | **12** | **97** | **5 : 45** | **205** | **1.2** | **34** |
| **XIIc** | **$C_{18}$** | **10** | **36** | **12.5** | **10** | **98** | **5 : 30** | **205** | **0.90** | **36.5** |

n = number of propylene oxide

Table (5): Biodegradability of oxypropenoxylated fatty acids:

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **Ia** | $C_{12}$ | 5 | 54 | 63.5 | 71 | 77 | 82 | 86 | - |
| **Ib** | $C_{12}$ | 7 | 51 | 62 | 70 | 74 | 80 | 87 | 91 |
| **Ic** | $C_{12}$ | 10 | 50 | 59 | 67 | 71 | 76 | 84 | 93 |
| **IIa** | $C_{14}$ | 5 | 51 | 59 | 68 | 76 | 83 | 87 | 94 |
| **IIb** | $C_{14}$ | 7 | 49 | 60 | 65 | 71 | 76 | 86 | 91 |
| **IIc** | $C_{14}$ | 10 | 48.5 | 57 | 62 | 69 | 73 | 81 | 89 |
| **IIIa** | $C_{18}$ | 5 | 36 | 47 | 58 | 64 | 69 | 82 | 93 |
| **IIIb** | $C_{18}$ | 7 | 35 | 45 | 56 | 61 | 68 | 76 | 85 |
| **IIIc** | $C_{18}$ | 10 | 32 | 41 | 53 | 59 | 65 | 74 | 83 |

n = number of propylene oxide

Table (6): Biodegradability of oxypropenoxylated dihydroxy fatty acids methyl ester:

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **IVa** | $C_{12}$ | 5 | 47.5 | 56 | 66 | 76 | 86 | 90 | 98 |
| **IVb** | $C_{12}$ | 7 | 46 | 54.5 | 63 | 75 | 83 | 88 | 97 |
| **IVc** | $C_{12}$ | 10 | 43 | 53 | 62 | 72 | 81.5 | 85 | 90 |
| **Va** | $C_{14}$ | 5 | 41 | 52 | 65 | 78 | 83 | 86.5 | 96 |
| **Vb** | $C_{14}$ | 7 | 38 | 53 | 63 | 74 | 80.5 | 85 | 93 |
| **Vc** | $C_{14}$ | 10 | 37 | 49 | 60.5 | 69 | 79 | 81 | 89 |
| **VIa** | $C_{18}$ | 5 | 34 | 44 | 56 | 67 | 78 | 81 | 88 |
| **VIb** | $C_{18}$ | 7 | 32 | 42 | 53 | 64 | 74 | 79 | 86.5 |
| **VIc** | $C_{18}$ | 10 | 31 | 39 | 51 | 62.5 | 74 | 76 | 82 |

n = number of propylene oxide

Table (7): Biodegradability of oxypropenoxylated fatty acids sulfates:

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **VIIa** | $C_{12}$ | 5 | 50 | 59 | 73 | 80 | 86 | 94 | - |
| **VIIb** | $C_{12}$ | 7 | 51 | 61 | 71 | 79 | 83 | 89 | - |
| **VIIc** | $C_{12}$ | 10 | 48 | 53 | 65 | 75 | 79 | 88 | 96 |
| **VIIIa** | $C_{14}$ | 5 | 49 | 61 | 71 | 79 | 84 | 92 | - |
| **VIIIb** | $C_{14}$ | 7 | 47 | 58 | 68 | 75 | 83 | 89 | 95 |
| **VIIIc** | $C_{14}$ | 10 | 49 | 55 | 61 | 72.5 | 78 | 86 | 93 |
| **IXa** | $C_{18}$ | 5 | 43 | 53 | 68 | 76 | 81 | 87 | 94 |
| **IXb** | $C_{18}$ | 7 | 46 | 51 | 65 | 74 | 88 | 86 | 91 |
| **IXc** | $C_{18}$ | 10 | 40 | 49 | 61 | 71 | 77 | 83 | 90 |

n = number of propylene oxide

Table (8): Biodegradability of oxypropenoxylated dihydroxy fatty acids methyl ester sulfates:

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| Xa | $C_{12}$ | 5 | 41 | 58 | 67 | 76 | 87 | 93 | - |
| Xb | $C_{12}$ | 7 | 40 | 54 | 62 | 74 | 83 | 91 | - |
| Xc | $C_{12}$ | 10 | 40 | 52.5 | 61 | 72 | 81 | 88 | 94 |
| XIa | $C_{14}$ | 5 | 38 | 52 | 63 | 73 | 84 | 91.5 | - |
| XIb | $C_{14}$ | 7 | 38 | 49 | 61 | 72 | 82 | 89 | - |
| XIc | $C_{14}$ | 10 | 37 | 44 | 59 | 69 | 81.5 | 88 | 92 |
| XIIa | $C_{18}$ | 5 | 34 | 48 | 58 | 67 | 77 | 86 | 91 |
| XIIb | $C_{18}$ | 7 | 32 | 46 | 56 | 65 | 74 | 83 | 90 |
| XIIc | $C_{18}$ | 10 | 29 | 40 | 51 | 61 | 69 | 80 | 88 |

n = number of propylene oxide

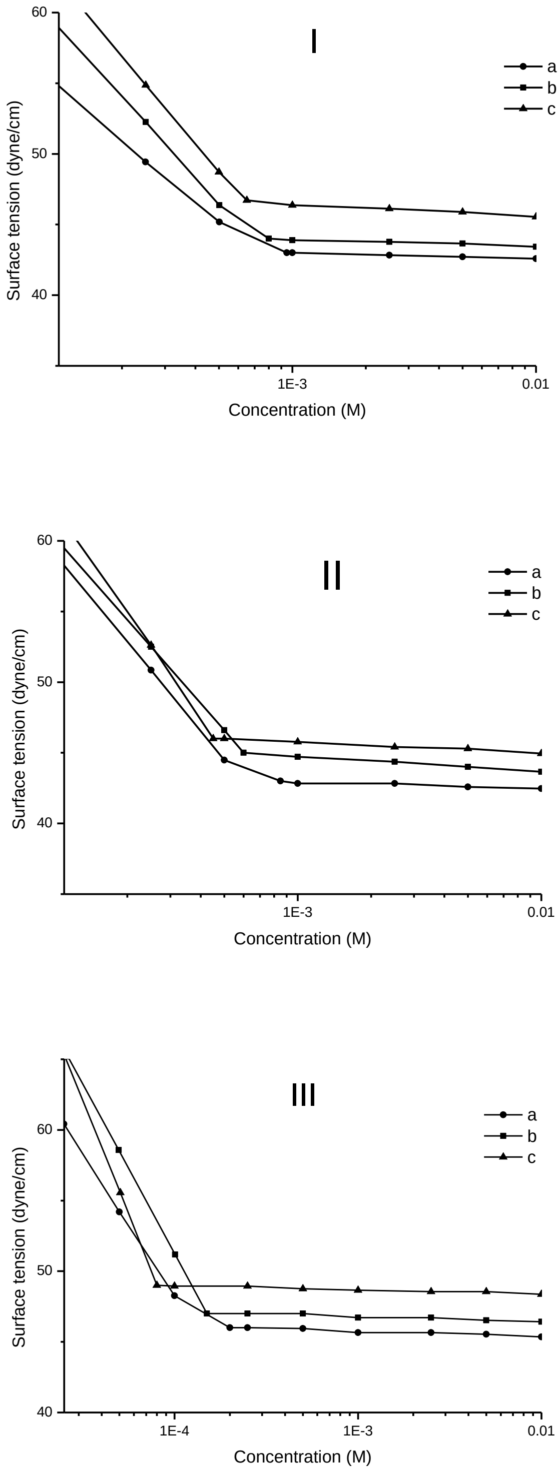


Fig. 52: The plot of surface tension versus the logarithmic molar surfactant concentration of the Ia-c – IIIa-c.

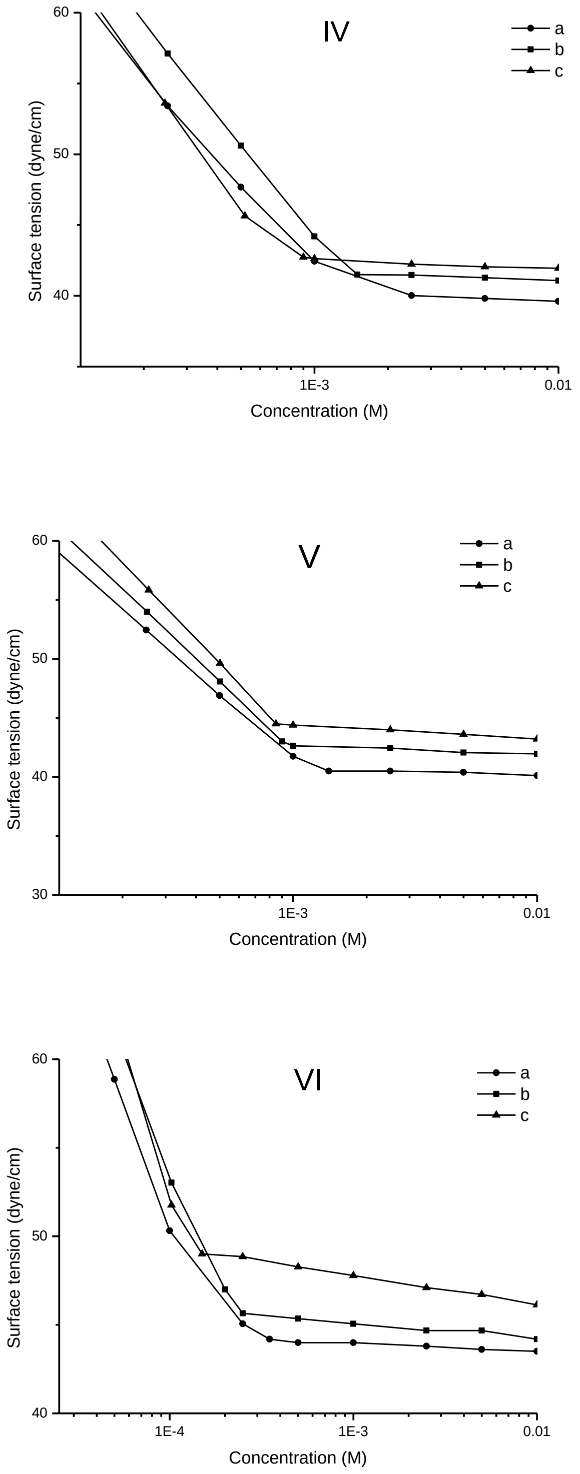


Fig. 53: The plot of surface tension versus the logarithmic molar surfactant concentration of the IVa-c – VIa-c.

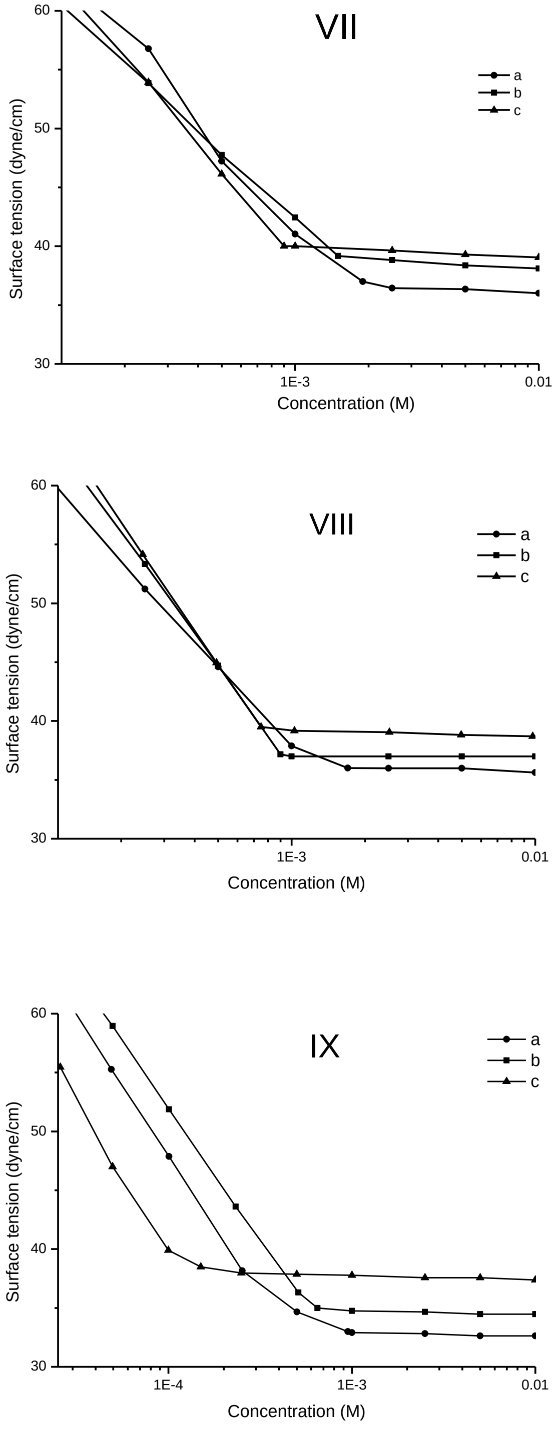


**Fig. 54: The plot of surface tension versus the logarithmic molar surfactant concentration of the VIIa-c – IXa-c.**

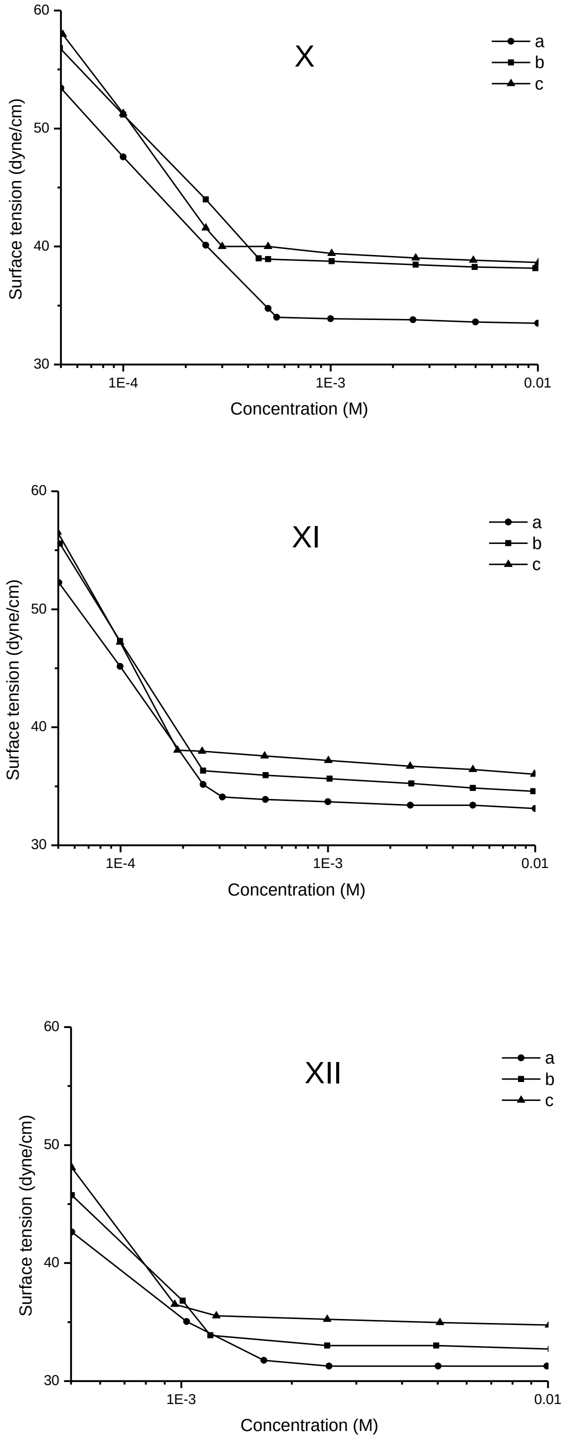


**Fig. 55: The plot of surface tension versus the logarithmic molar surfactant concentration of the Xa-c – XIIa-c.**

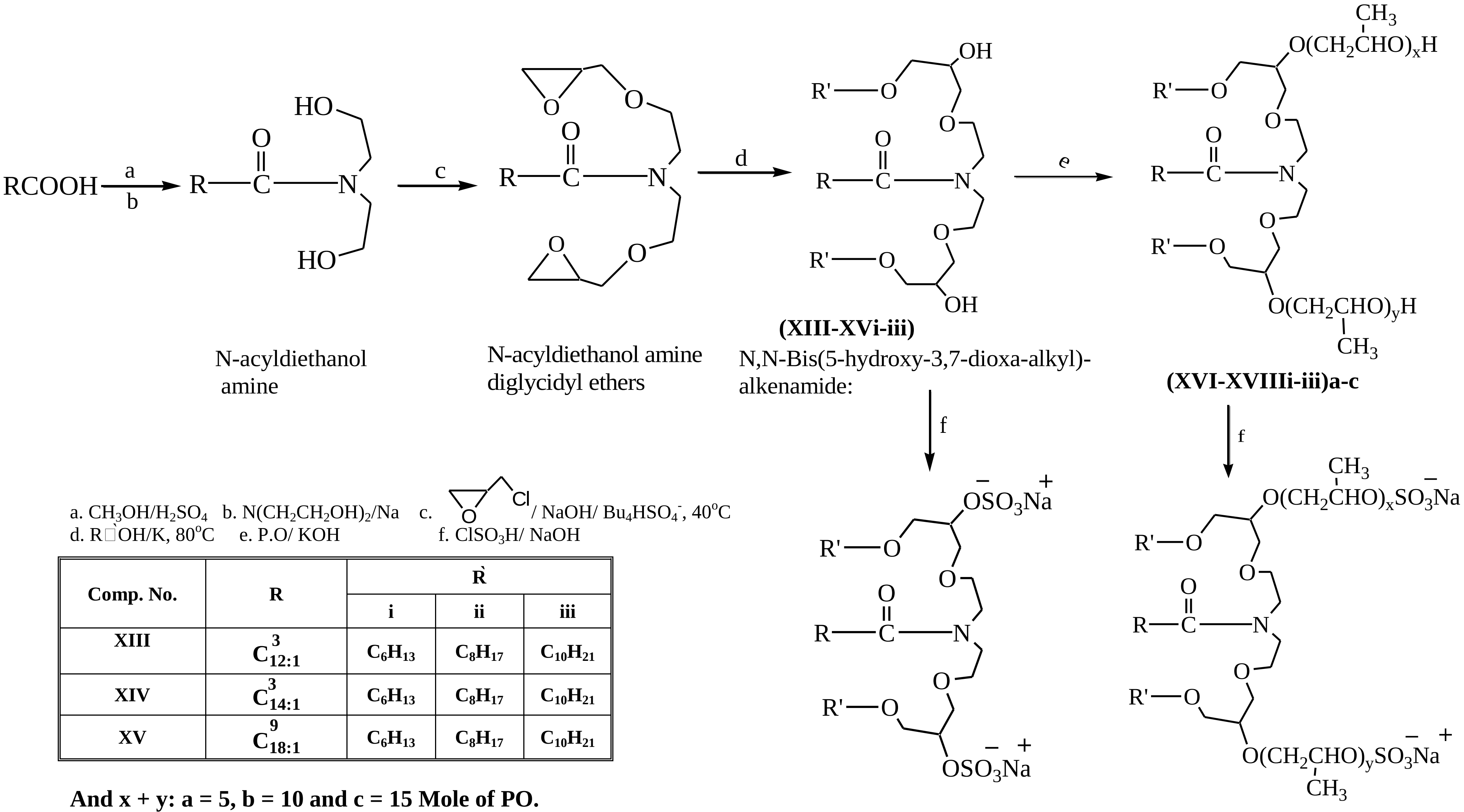
# Part (II)

## Synthesis and surface properties of gemini surfactants derived from N,N-bis(5-hydroxy-3, 7-dioxa-alkyl)-alkenamide:

Gemini surfactant is the family of surfactant molecules possessing more than one hydrophobic tail and hydrophilic head group. These surfactants usually have better surface-active properties than corresponding conventional surfactants of equal chain length. Geminis are used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property and vesicle formation.

This part will discuss the preparation and evaluation of three types of prepared gemini surfactants derived from N,N-bis(5-hydroxy-3,7-dioxa-alkyl)-alkenamide, as shown at (Scheme 2). The first type is a series of nonionic gemini surfactants synthesized by the proppenoxylaion of N,N-bis(5-hydroxy-3,7-dioxa-alkyl)-alkenamide. These nonionic Gemini surfactants were sulfated to produce nonionic-anionic gmini surfactants as a second type. The third type in a pure anionic surfactants prepared from the sulfation of N,N-bis(5-hydroxy-3,7-dioxa-alkyl)-alkenamide followed by neutralization by NaOH.

The surface properties, such as the surface and interfacial tension, cloud point, wetting time, foam height and emulsion stability, also the critical micelle concentration, CMC, have been determined for all the prepared surfactants.



N-acyldiethanol amine

N-acyldiethanol amine diglycidyl ethers

**(XIII-XVi-iii)**
N,N-Bis(5-hydroxy-3,7-dioxa-alkyl)-alkenamide:

**(XVI-XVIIIi-iii)a-c**

**(XXII-XXIVi-iii)**

(XIX-XXIi-iii)a-c

a. $CH_3OH/H_2SO_4$ b. $N(CH_2CH_2OH)_2$/Na c. / NaOH/ $Bu_4HSO_4^-$, 40°C
d. R′OH/K, 80°C e. P.O/ KOH f. $ClSO_3H$/ NaOH

| **Comp. No.** | **R** | **R`** | | |
|---|---|---|---|---|
| | | **i** | **ii** | **iii** |
| **XIII** | $C^{3}_{12:1}$ | $C_6H_{13}$ | $C_8H_{17}$ | $C_{10}H_{21}$ |
| **XIV** | $C^{3}_{14:1}$ | $C_6H_{13}$ | $C_8H_{17}$ | $C_{10}H_{21}$ |
| **XV** | $C^{9}_{18:1}$ | $C_6H_{13}$ | $C_8H_{17}$ | $C_{10}H_{21}$ |

**And x + y: a = 5, b = 10 and c = 15 Mole of PO.**

**Scheme 2**

## *II.a-Preparation of N-acyldiethanolamine:*

N-Acyldiethanolamine was synthesized by the reaction of diethanolamine with fatty acid methyl ester in the presence of a catalytic amount of metallic sodium in methanol. The amide product were confirmed by using IR spectra which show the characteristic band at 1638.9 $cm^{-1}$ characteristic for ν C=O of amide linkage (*cf.* fig. 12).

## *II.b-Preparation of N,N-bis(5,6-epoxy-3-oxahexyl)alken-amide:*

*N*-acyldiethanolamine diglycidyl ethers were prepared by the reaction of N-acyldiethanol amine with with epichlorohydrin under phase catalytic conditions using tetrabutyl ammonium bisulfate under vigorous stirring at $40^oC$ for 5 hours, methylene chloride (250 ml) was added to the reaction mixture, and insoluble solids were filtered off. After evaporation of the filtrate the product obtained as colourless liquid. IR showed the disappearance of OH band while it converted to ether linkage (*cf.* fig. 13).

## *II.c-Preparation of N,N-bis(5-hydroxy-3,7-dioxaalky)-alkenamide:*

Metallic potassium was dissolved into the alcohol (hexanol, octanol or decanol). N-acyldiethanolamine diglycidyl ethers were dropped carefully into the resulting solution. The reaction mixture was then stirred for 12 hr at 80o. After neutralization with 10% hydrochloric acid, the reaction mixture was extracted with a methylene chloride: water solvent system. After the organic extracts were combined and dried with $MgSO_4$, any excess of alcohol was distilled off under reduced pressure. All the products compounds were obtained as a colourless liquid. The *N*,*N*-bis(5-hydroxy-3,7-dioxaheptadecyl)-3-dodecenamide, *N*,*N*-bis(5-hydroxy-3,7-dioxapentadecyl)-3-tetradecenamide and *N*,*N*-bis(5-hydroxy-3,7-dioxatridecyl)-9-octadecenamide (XIIIiii, XIVii and XVi respectively) were investigated by using IR and $^1$H-NMR spectra. The data of IR and $^1$H-NMR shown in table 9, Figures 14-16 showed the IR spectra and the others from 41-43 showed the $^1$H-NMR spectra.

| Comp. No. | R | R̀ | $^1$H-NMR (δ) | IR |
|---|---|---|---|---|
| XIIIiii | $C^{3}_{12:1}$ | $C_{10}H_{21}$ | 0.72 [t, 9H, terminal(-$CH_3$)], 1.16-1.46 [m, 46H, (-$CH_2$) of alkyl chain], 1.91 [s, 2H (-OH)], 2.87 [s, 2H, =CH-$\underline{CH_2}$-C=O], 3.02-3.70 [m, 20H, (-$CH_2$O)], 3.84 [s, 2H, 2(-$\underline{CH}$OH)], 5.40 [m, 2H, (-$\underline{CH}$=$\underline{CH}$-)]. | 3425 $cm^{-1}$ (ν –OH), 2926, 2854 $cm^{-1}$ (ν –CH- aliphatic), 1624 $cm^{-1}$ (ν –C=O amide), 1465 $cm^{-1}$ (ν –$CH_3$ bending) and 1173 $cm^{-1}$ (ν –O– ether linkage) |
| XIVii | $C^{3}_{14:1}$ | $C_8H_{17}$ | 0.72 [t, 9H, terminal(-$CH_3$)], 1.16-1.46 [m, 42H, (-$CH_2$) of alkyl chain], 1.91 [s, 2H (-OH)], 2.87 [s, 2H, =CH-$\underline{CH_2}$-C=O], 3.27-3.70 [m, 20H, (-$CH_2$O)], 3.90 [s, 2H, 2(-$\underline{CH}$OH)], 5.40 [m, 2H, (-$\underline{CH}$=$\underline{CH}$-)]. | 3361 $cm^{-1}$ (ν –OH), 2924, 2853 $cm^{-1}$ (ν –CH- aliphatic), 1637 $cm^{-1}$ (ν –C=O amide), 1464 $cm^{-1}$ (ν –$CH_3$ bending) and 1124 $cm^{-1}$ (ν –O– ether linkage) |
| XVi | $C^{9}_{18:1}$ | $C_6H_{13}$ | 0.78 [t, 9H, terminal(-$CH_3$)], 0.88-1.51 [m, 42H, (-$CH_2$) of alkyl chain], 1.91 [s, 2H (-OH)], 2.24 [t, 2H, -$\underline{CH_2}$-C=O], 3.35-3.59 [m, 20H, (-$CH_2$O)], 3.94 [t, 2H, 2(-$\underline{CH}$OH)], 5.26 [m, 2H, (-$\underline{CH}$=$\underline{CH}$-)]. | 3363 $cm^{-1}$ (ν –OH), 2925, 2856 $cm^{-1}$ (ν –CH- aliphatic), 1649 $cm^{-1}$ (ν –C=O amide), 1463 $cm^{-1}$ (ν –$CH_3$ bending) and 1056 $cm^{-1}$ (ν –O– ether linkage) |

**Table 9: spectral data of compounds XIIIiii, XIVii and XVi.**

## *II.d -Nonionic gemini surfactants:*

Many nonionic gemini surfactants have been reported in the literature over the last years. A large number of these have been synthesised with sugar based head groups. Also polyoxyethylene gemini surfactants have been studied to a lesser degree than sugar based nonionic gemini surfactants. There is no any of nonionic gemini surfactant prepared by using polypropylene glycol mentioned before.

The *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-alkenamide compounds were reacted with propylene oxide with different molar ratio (n = 5,10 and 15 mole) in the presence of KOH to give oxypropenoxylated products (XVI-XVIIIi-iii)$_{a\text{-}c}$. The structures of the prepared nonionic surfactants were confirmed by using IR and $^1$H-NMR spectra, The IR spectrum of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxatridecyl)-3-dodecenamide (5 ,10 and 15 mole) (XVIiiia-c) (Fig. 17-19), all these figures showed characteristic bands of the ether linkage of polypropenoxy chain (ν C-O-C) at 1100-1120 cm$^{-1}$ and at 1636 cm$^{-1}$ characteristic for ν –C=O of amide group. $^1$H-NMR spectra showed that, the characteristic protons of propenoxy group at $\delta$ = 3.29-3.98 ppm (*cf.* Fig 44).

## *Surface active properties:*

The surface active properties of the prepared nonionic gemini surfactant were determined.

### 1- Surface and Interfacial tensions :

The surface and interfacial tension of the prepared oxypropenoxylated gemini nonionic surfactants (XVI-XVIIIi-iii)a-c are given in (tables 11-13). It showed that, the values of surface and interfacial tension increases as the mass of hydrophilic groups increase within the range under study. Also, it increases as the hydrophobic part increase. Compounds (XVI-XVIIi-iii)a-c showed a lower value of surface and interfacial tension than those of (XVIIIi-iii)a-c.

## 2- Cloud point :

Tables 11-13 summarize the clouding behaviour of 1 wt% gemini surfactant solutions. All the prepared gemini nonionic surfactants with 5 mole of propylene oxide are turbid at room temperature (30$^{o}$C) and its solubility improved by increasing the number of moles of propylene oxide. Nonionic gemini surfactants prepared from 9-octadecanoic acid showed very low cloud point because the increasing hydrophobicity may make the molecule insoluble. The trends of decreasing Cloud point with increasing alkyl chain length and increasing the degree of propenoxylation is parallel in the behaviour as the conventional surfactants.

## 3- Wetting time :

The wetting properties of 1.0 % solutions in distilled water were measured. All the synthesized nonionic gemini surfactants show increase in the wetting time with increasing the number of propylene oxide units per hydrophobic molecule, also it found that the compounds (XVIIIi-iii)a-c have a higher wetting time than other compounds.

## 4- Emulsifying properties :

The emulsifying properties increased with decreasing the number of propylene oxide units into the molecule. Also the emulsifying properties increased with increasing the alkyl chain length. It noticed that the emulsifying properties of nonionic gemini surfactants are higher than those of conventional surfactants as shown in (tables 11-13).

## 5- Foaming Power :

As mentioned before the nonionic surfactants have low and unstable foam. On the other hand the foam height of the prepared surfactants has very low foam and it slightly increases with increasing the propylene oxide unit per molecule, while the compounds with 5 mole of propylene oxide gave no foam.

## 6- Critical micelle concentration *(CMC)* :

The variation in surface tension of aqueous solutions of compounds (XVI-XVIIIi-iii)a-c versus, surfactant concentration, plotted as its logarithm to determine the break point indicates the *CMC*. The values of the *CMC* were collected in the tables 11-13. It is found that the *CMC* decreases as the propylene oxide number increases, as expected from the fact that the polypropylene oxide chain is globally lipophilic(201). The increase in carbon number in the nonpolar chain increase lipohilicity with decrease the *CMC* (*cf.* figures 56-58).

The *CMCs* values are between $10^{-7}$ and $10^{-6}$ M, and they are very low compared to the most common conventional nonionic surfactant.

## 7- Biodegradability :

The biodegradation of all the prepared nonionic gemini surfactants (XVI-XVIIIi-iii)$_{a\text{-}c}$ are recorded in (tables 18- 20), where the biodegradation is expressed by decreasing the surface tension with time (day). The result indicate that, the biodegradability decreased with the increasing of the propenoxy groups, also it showed lower biodegradability values than conventional nonionic surfactants.

## II.e - Anionic-nonionic gemini surfactants:

The prepared nonionic gemini surfactants of the polyoxypropylene, have poor foam, seldom solubility and gave cloudy solutions at lower temperature. To improve the surface properties of these surfactants, they sulfated with chlorosulfonic acid and neutralized with sodium hydroxide, to give the anionic-nonionic gemini surfactants (XIX-XXIi-iii)a-c. These surfactants expect to have both properties of nonionic and anionic surfactants.

## Surface active properties:

The surface activity and related properties of the prepared anionic-nonionic surfactants are given in (tables 14-16).

### 1- Surface and Interfacial tensions :

The surface and interfacial tension of the prepared oxypropenoxylated gemini anionic-nonionic surfactants (XIX-XXIi-iii)a-c are given in (tables 14-16). The modification of nonionic gemini surfactants to anionic-nonionic gemini surfactants has been found to be more effective and efficient than the corresponding nonionic gemini surfactants at lowering the surface tension of water. Also, it showed that the compound (XXIi-iii)a-c have lower surface tension than other prepared compounds.

### 2- Kraft point :

Tables 14-16 showed the kraft points of the prepared surfactants. It showed that; all the types of these surfactants were freely soluble in water at 1 wt % concentration and the kraft point of the compounds (XIX-XXi-iii)a-c are below $0^oC$, while the kraft point of (XXIi-iii)a-c higher than $0^oC$, and it also decreased with increasing the number of propylene oxide units in the molecule.

## 3- Wetting time :

The wetting time of the gemini anionic-nonionic surfactants (XIX-XXIi-iii)a-c which listed in (tables 14-16), showed that, the wetting time of sulphated compounds have better wetting time than those of gemini nonionic surfactants. On the other hand the wetting time slightly increase as the number of carbon atoms increase, and the increase of propylene oxide units in the molecule causes the increasing of the wetting time.

## 4- Emulsifying properties :

Studies are still being carried out on the utilization of surfactants in emulsion formation, The data are in (tables 14-16) showed the emulsifying properties increased with increasing the alkyl chain length and with decreasing the number of propylene oxide units. As in conventional surfactants the oxypropenoxylated compounds (XVI-XVIIIi-iii)a-c showed higher values of emulsion stability than that of (XIX-XXIi-iii)a-c and better emulsifying properties.

## 5- Foaming power :

The efficiency of the synthesized surfactants as foamier increases with increase the alkyl chain length. Where it decreases with increasing the percent of propylene oxide units in the molecule. The foam height of these compounds is higher than those of nonionic surfactants (XVI-XVIIIi-iii)a-c.

## 6- Critical micelle concentration *(CMC)* :

Figures 59-61 show the variations in surface tension of aqueous solutions of compounds (XIX-XXIi-iii)a-c versus surfactant concentration, to determine the *CMC* values. The values of *CMC* and the surface tension at *CMC* are listed in tables 14-16, It is reveal that the gemini anionic–nonionic surfactant (XIX-XXIi-iii)a-c has a higher *CMC* value than that of the gemini nonionic surfactant (XVI-XVIIIi-iii)a-c.

As in conventional surfactants the *CMC* values in tables 14-16, indicate that an increase in the propylene glycol intermediate chain length tended to reduce the CMC(112), and also shifts to lower concentration with increasing hydrocarbon chain length(147).

**7- Biodegradability :**

The data of biodegradability of (XIX-XXIi-iii)a-c surfactant listed in (Tables 21-23), it is seen that, the rate of biodegradion was decreasing with increasing the number of carbon atoms in the alkyl chain. It also introduce that the compounds (XIX-XXIi-iii)a-c are more biodegradable than those gemini nonionic surfactants.

## *II.f - Anionic gemini surfactants:*

The majority of gemini surfactant studies have been on ionic systems. Anionic gemini surfactants are interested one in these compounds, both academic and industrial detergency.

Bis(sulfate) types of amphipathic compounds with three long-chain alkyl groups were prepared by the reaction of N-(long-chain acyl) diethanolamine diglycidyl ethers with long-chain fatty alcohols, followed by sulfation with chlorosulfonic acid then neutralized with NaOH. The synthetic route for this triple-chain surfactants (XXII-XXIV) i-iii is shown in scheme 2. These surfactants were confirmed by elemental analysis listed in (table 10).

## *Surface active properties:*

The surface active properties given in table 17 shows that, the products obtained have pronounced surface activity.

**1- Surface and Interfacial tensions :**

The surface and interfacial tension of (XXII-XXIV)i-iii were much smaller than those of corresponding anionic-nonionic and nonionic gemini surfactants. The values of (XXIV)i-iii were below than 30 dyne $cm^{-1}$ and they exhibit the maximum ability to lower the surface tension among the compounds in this work. This gemini anionic surfactants (XXII-XXIV) i-iii show high efficiency in lowering the surface tension of water, and interfacial tension at the oil/water interface.

## 2- Kraft point :

All these sodium disulfates (XXII-XXIV)i-iii were readily soluble in water, and they have excellent hydrophilicity for practical because the kraft point of all compounds was below $0^{o}C$.

## 3- Wetting time :

The wetting time of this gemini anionic surfactants (XXII-XXIV) i-iii are listed in (table 17). Wetting times for surfactants XXIVi-iii are much slower than the wetting time of (XXII-XXIII)i-iii.

On the other hand the wetting time slightly increase as the number of carbon atoms increase. The compounds (XXII-XXIV)i-iii can be considered as good wetting agent.

## 4- Emulsifying properties :

All the prepared anionic Gemini surfactants show lower emulsion stability compared with those of nonionic gemini surfactants.

## 5- Foaming power :

The values of the foaming height were investigated to the prepared compounds and the result is given in table 17. The prepared gemini anionic surfactants recorded higher values of foaming heights.

## 6- Critical micelle concentration *(CMC)* :

The critical micelle concentration, determined from the break point of each curve in (Fig. 62). The values of *CMC* and the surface tension at *CMC* are listed in (table 17), The results show that, the gemini surfactants (XXII-XXIII)i-iii show higher *CMC* than (XXIV)i-iii.

The *CMC* values of prepared gemini surfactants showed that, the anionic gemini surfactant has a higher *CMC* value than that of the anionic–nonionic gemini surfactant (tables 11- 17), this may be due to the anionic surfactant has a stronger repulsive electrostatic nature of the polar group than the static hydration requirement of the propylene oxides in an anionic–nonionic surfactant moiety(202).

## 7- Biodegradability :

The biodegradability of tested compounds after one week was determined and listed in table 24. the result obtained indicated that, all the compounds had a much higher biodegradability. Compounds (XXII-XXIII)i-iii are much easily biodegradable than (XXIV)i-iii.

Table (10) : Elemental analysis of *N*,*N*-bis(5-hydroxy-3,7-dioxa-alky)-alkenamide sulfates:

| Comp. No. | M. Formula | M. Wt. | C% | | H% | | N% | | S% | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| XXIIi | $C_{34}H_{65}NO_{13}S_2 Na_2$ | 805.99 | 50.67 | 50.12 | 8.13 | 7.88 | 1.74 | 1.37 | 7.96 | 7.56 |
| XXIIii | $C_{38}H_{73}NO_{13}S_2 Na_2$ | 862.10 | 52.94 | 52.67 | 8.53 | 8.14 | 1.62 | 1.33 | 7.44 | 7.01 |
| XXIIiii | $C_{42}H_{41}NO_{13}S_2 Na_2$ | 918.20 | 54.94 | 54.59 | 8.89 | 8.47 | 1.53 | 1.26 | 6.98 | 6.47 |
| XXIIIi | $C_{36}H_{69}NO_{13}S_2 Na_2$ | 834.04 | 51.84 | 51.29 | 8.34 | 7.99 | 1.68 | 1.29 | 7.69 | 7.28 |
| XXIIIii | $C_{40}H_{77}NO_{13}S_2 Na_2$ | 890.15 | 53.97 | 53.59 | 8.72 | 8.44 | 1.57 | 1.49 | 7.20 | 7.06 |
| XXIIIiii | $C_{44}H_{85}NO_{13}S_2 Na_2$ | 946.26 | 55.85 | 55.36 | 9.05 | 9.02 | 1.48 | 1.33 | 6.78 | 6.35 |
| XXIVi | $C_{40}H_{77}NO_{13}S_2 Na_2$ | 890.15 | 53.97 | 53.29 | 8.72 | 8.30 | 1.57 | 1.39 | 7.20 | 6.95 |
| XXIVii | $C_{44}H_{85}NO_{13}S_2 Na_2$ | 946.29 | 55.85 | 55.41 | 9.05 | 8.75 | 1.48 | 1.27 | 6.78 | 6.34 |
| XXIViii | $C_{48}H_{93}NO_{13}S_2 Na_2$ | 1002.36 | 57.52 | 57.24 | 9.35 | 9.09 | 1.40 | 1.13 | 6.40 | 6.12 |

Table(11): **Surface properties of oxypropenoxylated *N*,*N*-bis(5-hydroxy-3,7-dioxa-alky)-dodec-3-enamide:**

| Compound No. | Ȓ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XVIi-a | $C_6$ | 5 | 39 | 9 | 30 | 55 | 80 | - | 0.92 | 40 |
| XVIi-b | $C_6$ | 10 | 39.5 | 11 | 45 | 75 | 73 | 40 | 0.80 | 41 |
| XVIi-c | $C_6$ | 15 | 41 | 12 | 53 | 90 | 69 | 55 | 0.50 | 43 |
| XVIii-a | $C_8$ | 5 | 40 | 10.5 | 30 | 83 | 75 | 30 | 0.80 | 41.5 |
| XVIii-b | $C_8$ | 10 | 41 | 11 | 42 | 99 | 71 | 40 | 0.60 | 43 |
| XVIii-c | $C_8$ | 15 | 42.5 | 13 | 51 | 115 | 65 | 50 | 0.35 | 44 |
| XVIiii-a | $C_{10}$ | 5 | 41 | 11.5 | 30 | 87 | 94 | - | 0.55 | 42 |
| XVIiii-b | $C_{10}$ | 10 | 42 | 12 | 39 | 106 | 83 | 20 | 0.30 | 44 |
| XVIiii-c | $C_{10}$ | 15 | 43.5 | 13.5 | 47 | 121 | 73 | 30 | 0.10 | 46 |

**n = number of PO. units**

Table(12): **Surface properties of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-tetradec-3-en-amide:**

| Compound No. | Ř | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XVIIi-a | $C_6$ | 5 | 40 | 11 | 30 | 80 | 80 | - | 0.80 | 41 |
| XVIIi-b | $C_6$ | 10 | 41 | 13 | 40 | 98 | 76 | 30 | 0.61 | 43 |
| XVIIi-c | $C_6$ | 15 | 42.5 | 14.5 | 51 | 100 | 74 | 50 | 0.35 | 44 |
| XVIIii-a | $C_8$ | 5 | 42 | 12 | 30 | 95 | 90 | - | 0.65 | 43.5 |
| XVIIii-b | $C_8$ | 10 | 43 | 13 | 39 | 105 | 85 | 40 | 0.62 | 45 |
| XVIIii-c | $C_8$ | 15 | 43.5 | 15 | 48 | 120 | 72 | 50 | 0.25 | 46.5 |
| XVIIiii-a | $C_{10}$ | 5 | 42 | 11 | 30 | 109 | 90 | - | 0.34 | 43 |
| XVIIiii-b | $C_{10}$ | 10 | 45 | 13.5 | 39 | 99 | 91 | 45 | 0.20 | 46.5 |
| XVIIiii-c | $C_{10}$ | 15 | 46 | 14 | 43 | 130 | 82 | 60 | 0.13 | 48 |

**n = number of PO. units**

Table (13) : **Surface properties of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-octadec-9-en-amide:**

| Compound No. | Ŕ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XVIIIi-a | $C_6$ | 5 | 44 | 12 | 30 | 120 | 99 | - | 0.35 | 45 |
| XVIIIi-b | $C_6$ | 10 | 45 | 14 | 39 | 133 | 81 | 45 | 0.20 | 47 |
| XVIIIi-c | $C_6$ | 15 | 47 | 15.5 | 48 | 145 | 75 | 50 | 0.12 | 49 |
| XVIIIii-a | $C_8$ | 5 | 45.5 | 13 | 30 | 137 | 91 | - | 0.21 | 47 |
| XVIIIii-b | $C_8$ | 10 | 48 | 14.5 | 39 | 157 | 84 | 20 | 0.10 | 49.5 |
| XVIIIii-c | $C_8$ | 15 | 49 | 16 | 43 | 160 | 79 | 35 | 0.08 | 50.5 |
| XVIIIiii-a | $C_{10}$ | 5 | 47 | 14 | 30 | 151 | 98 | - | 0.15 | 49 |
| XVIIIiii-b | $C_{10}$ | 10 | 48 | 16 | 30 | 170 | 89 | - | 0.07 | 49.5 |
| XVIIIiii-c | $C_{10}$ | 15 | 49.5 | 17 | 40 | 175 | 80 | 40 | 0.05 | 51 |

**n = number of PO. units**

Table (14) : **Surface properties of oxypropenoxylated *N*,*N*-bis(5-hydroxy-3,7-dioxa-alky)-dodec-3-enamide sulfates:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point $^{o}$C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XIXi-a | $C_6$ | 5 | 35.5 | 10.5 | $< 0$ | 40 | 5 : 30 | 160 | 2.8 | 36 |
| XIXi-b | $C_6$ | 10 | 37 | 11.5 | $< 0$ | 42 | 4 : 55 | 130 | 2.0 | 38.5 |
| XIXi-c | $C_6$ | 15 | 39 | 12.5 | $< 0$ | 45 | 4 : 34 | 120 | 1.5 | 41 |
| XIXii-a | $C_8$ | 5 | 35 | 9 | $< 0$ | 43 | 5 : 50 | 160 | 2.3 | 36 |
| XIXii-b | $C_8$ | 10 | 37 | 10.5 | $< 0$ | 44 | 5 : 31 | 150 | 1.7 | 39 |
| XIXii-c | $C_8$ | 15 | 37.5 | 12 | $< 0$ | 49 | 5 : 25 | 135 | 1.1 | 41.5 |
| XIXiii-a | $C_{10}$ | 5 | 34 | 8.5 | $< 0$ | 45 | 6 : 33 | 200 | 1.1 | 35 |
| XIXiii-b | $C_{10}$ | 10 | 34.5 | 10.5 | $< 0$ | 48 | 6 : 11 | 185 | 0.90 | 37.5 |
| XIXiii-c | $C_{10}$ | 15 | 38 | 12 | $< 0$ | 53 | 5 : 55 | 165 | 0.83 | 40 |

**n = number of PO. units**

Table (15): **Surface properties of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-tetradec-3- enamide sulfates:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXi-a | $C_6$ | 5 | 36 | 10 | < 0 | 42 | 5 : 25 | 160 | 1.8 | 36 |
| XXi-b | $C_6$ | 10 | 36.5 | 11 | < 0 | 44 | 5 : 05 | 165 | 1.4 | 38 |
| XXi-c | $C_6$ | 15 | 38 | 11.5 | < 0 | 51 | 4 : 54 | 130 | 1.0 | 40.5 |
| XXii-a | $C_8$ | 5 | 34 | 9 | < 0 | 42 | 6 : 25 | 180 | 1.5 | 35 |
| XXii-b | $C_8$ | 10 | 35 | 10 | < 0 | 46 | 6 : 00 | 170 | 0.95 | 36.5 |
| XXii-c | $C_8$ | 15 | 36.5 | 10.5 | < 0 | 54 | 6 : 49 | 155 | 0.83 | 40 |
| XXiii-a | $C_{10}$ | 5 | 33 | 9 | < 0 | 45 | 6 : 50 | 210 | 0.90 | 34 |
| XXiii-b | $C_{10}$ | 10 | 33.5 | 10.5 | < 0 | 50 | 6 : 31 | 200 | 0.80 | 35 |
| XXiii-c | $C_{10}$ | 15 | 35 | 11 | < 0 | 58 | 6 : 27 | 180 | 0.68 | 39 |

**n = number of PO. units**

Table (16): **Surface properties of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-octadec-9-enamide sulfates:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXIi-a | $C_6$ | 5 | 33 | 10 | 7 | 47 | 6 : 10 | 180 | 0.68 | 34.5 |
| XXIi-b | $C_6$ | 10 | 34 | 11.5 | 5 | 50 | 6 : 25 | 170 | 0.55 | 35.5 |
| XXIi-c | $C_6$ | 15 | 35.5 | 12 | 4 | 56 | 6 : 10 | 150 | 0.40 | 38 |
| XXIii-a | $C_8$ | 5 | 31 | 8 | 9 | 64 | 6 : 49 | 200 | 0.61 | 33.5 |
| XXIii-b | $C_8$ | 10 | 32 | 10.5 | 6 | 52 | 6 : 65 | 180 | 0.45 | 35.5 |
| XXIii-c | $C_8$ | 15 | 34 | 11.5 | 6 | 55 | 6 : 10 | 170 | 0.40 | 37 |
| XXIiii-a | $C_{10}$ | 5 | 31 | 8.5 | 8 | 52 | 7 : 11 | 220 | 0.35 | 33 |
| XXIiii-b | $C_{10}$ | 10 | 33 | 9 | 7 | 56 | 7 : 00 | 210 | 0.25 | 34 |
| XXIiii-c | $C_{10}$ | 15 | 33.5 | 10.5 | 5 | 59 | 6 : 51 | 195 | 0.18 | 35 |

**n = number of PO. units**

Table (17) : **Surface properties of *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-alkenamide sulfates:**

| Compound No. | R | R̀ | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-5}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXIIi | $C_{12}$ | $C_6$ | 32.5 | 10 | $< 0$ | 61 | 3 : 20 | 260 | 7.0 | 33.5 |
| XXIIi | $C_{12}$ | $C_8$ | 32 | 8 | $< 0$ | 65 | 3 : 40 | 270 | 6.1 | 32.5 |
| XXIIi | $C_{12}$ | $C_{10}$ | 29 | 7 | $< 0$ | 65 | 3 : 50 | 290 | 5.0 | 30 |
| XXIIIii | $C_{14}$ | $C_6$ | 31 | 11 | $< 0$ | 54 | 4 : 20 | 270 | 6.0 | 33 |
| XXIIIii | $C_{14}$ | $C_8$ | 28 | 10 | $< 0$ | 67 | 4 : 30 | 290 | 5.5 | 29.5 |
| XXIIIii | $C_{14}$ | $C_{10}$ | 27 | 8 | $< 0$ | 64 | 4 : 30 | 300 | 4.0 | 28 |
| XXIViii | $C_{18}$ | $C_6$ | 29 | 11 | $< 0$ | 78 | 4 : 25 | 280 | 1.7 | 31 |
| XXIViii | $C_{18}$ | $C_8$ | 28 | 9 | $< 0$ | 95 | 4 : 40 | 300 | 1.2 | 29.5 |
| XXIViii | $C_{18}$ | $C_{10}$ | 25 | 10 | $< 0$ | 102 | 5 : 00 | 350 | 0.80 | 27 |

Table (18) : **Biodegradability of Surface properties of oxypropenoxylated N,N-bis(5-hydroxy-3,7-dioxa-alky)-dodec-3-enamide:**

| Compound No. | R̀ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **XVIi-a** | $C_6$ | 5 | 44 | 54 | 61 | 64 | 73 | 81 | 88 |
| **XVIi-b** | $C_6$ | 10 | 41 | 51 | 54 | 63 | 70 | 79 | 87 |
| **XVIi-c** | $C_6$ | 15 | 35 | 50 | 53 | 60 | 67 | 78 | 85 |
| **XVIii-a** | $C_8$ | 5 | 43 | 51 | 57 | 63 | 70 | 77 | 84 |
| **XVIii-b** | $C_8$ | 10 | 39 | 50 | 56 | 62 | 67 | 75 | 82 |
| **XVIii-c** | $C_8$ | 15 | 36 | 44 | 52 | 60 | 65 | 74 | 81 |
| **XVIiii-a** | $C_{10}$ | 5 | 38 | 48 | 55 | 60 | 68 | 73 | 83 |
| **XVIiii-b** | $C_{10}$ | 10 | 36 | 46 | 54 | 59 | 66 | 72 | 77 |
| **XVIiii-c** | $C_{10}$ | 15 | 31 | 43 | 49 | 56 | 64 | 68 | 75 |

**n = number of PO. units**

Table (19) : **Biodegradability of Surface properties of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-tetradec-3-enamide:**

| Compound No. | Ȓ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XVIIi-a | $C_6$ | 5 | 41 | 51 | 58 | 69 | 72 | 81 | 86 |
| XVIIi-b | $C_6$ | 10 | 38 | 48 | 56 | 67 | 71 | 75 | 83 |
| XVIIi-c | $C_6$ | 15 | 31 | 46 | 51 | 59 | 65 | 74 | 80 |
| XVIIii-a | $C_8$ | 5 | 41 | 50 | 56 | 61 | 68 | 79 | 80 |
| XVIIii-b | $C_8$ | 10 | 36 | 46 | 53 | 58 | 67 | 72 | 81 |
| XVIIii-c | $C_8$ | 15 | 35 | 43 | 54 | 57 | 63 | 70 | 77 |
| XVIIiii-a | $C_{10}$ | 5 | 36 | 46 | 51 | 58 | 65 | 71 | 79 |
| XVIIiii-b | $C_{10}$ | 10 | 35 | 44 | 49 | 56 | 62 | 70 | 76 |
| XVIIiii-c | $C_{10}$ | 15 | 30 | 42 | 48 | 53 | 61 | 66 | 74 |

**n = number of PO. units**

Table (20) : **Biodegradability of Surface properties of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-octadec-9-enamide:**

| Compound No. | R̀ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XVIIIi-a | $C_6$ | 5 | 39 | 46 | 58 | 60 | 69 | 73 | 78 |
| XVIIIi-b | $C_6$ | 10 | 37 | 45 | 53.5 | 59 | 67 | 70 | 76 |
| XVIIIi-c | $C_6$ | 15 | 32 | 39 | 51 | 56 | 64 | 68 | 75 |
| XVIIIii-a | $C_8$ | 5 | 34 | 44 | 53 | 57.5 | 66 | 69.5 | 76 |
| XVIIIii-b | $C_8$ | 10 | 32 | 43 | 48.5 | 56 | 64 | 68 | 74 |
| XVIIIii-c | $C_8$ | 15 | 30 | 41 | 47 | 53 | 61.5 | 65 | 73 |
| XVIIIiii-a | $C_{10}$ | 5 | 32 | .9 | 44 | 52 | 65 | 70 | 74 |
| XVIIIiii-b | $C_{10}$ | 10 | 30 | 36.5 | 43 | 50 | 64 | 68 | 71 |
| XVIIIiii-c | $C_{10}$ | 15 | 28 | 36 | 42 | 54 | 61 | 67 | 69 |

**n = number of PO. units**

Table (21) : **Biodegradability of oxypropenoxylated *N*,*N*-bis(5-hydroxy-3,7-dioxa-alky)-dodec-3-enamide sulfates:**

| Compound No. | Ȓ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XIXi-a | $C_6$ | 5 | 45 | 56 | 64 | 71 | 79 | 84 | 95 |
| XIXi-b | $C_6$ | 10 | 41 | 53 | 59 | 68 | 79 | 83 | 93 |
| XIXi-c | $C_6$ | 15 | 39 | 49.5 | 56 | 68 | 76.5 | 82 | 89 |
| XIXii-a | $C_8$ | 5 | 46 | 55 | 61 | 69 | 78 | 84 | 95 |
| XIXii-b | $C_8$ | 10 | 43 | 52 | 58 | 67 | 75 | 81 | 92 |
| XIXii-c | $C_8$ | 15 | 40 | 48 | 56 | 64 | 73.5 | 79 | 90 |
| XIXiii-a | $C_{10}$ | 5 | 43 | 53 | 62 | 72 | 76 | 81 | 93 |
| XIXiii-b | $C_{10}$ | 10 | 40 | 51 | 60 | 69 | 73 | 78 | 89 |
| XIXiii-c | $C_{10}$ | 15 | 36 | 44 | 53.5 | 63 | 71.5 | 76 | 87 |

**n = number of PO. units**

Table (22) : **Biodegradability of oxypropenoxylated *N*,*N*-bis(5-hydroxy-3,7-dioxa-alky)-tetradec-3-enamide sulfates:**

| Compound No. | Ȓ | n | $1^{st}$ day | $2^{nd}$ day | $3^{rd}$ day | $4^{th}$ day | $5^{th}$ day | $6^{th}$ day | $7^{th}$ day |
|---|---|---|---|---|---|---|---|---|---|
| XXi-a | $C_6$ | 5 | 44 | 56 | 63 | 68 | 80 | 83 | 95 |
| XXi-b | $C_6$ | 10 | 39 | 52 | 62 | 68 | 78 | 81 | 90 |
| XXi-c | $C_6$ | 15 | 37 | 51 | 51 | 63 | 73 | 80 | 87 |
| XXii-a | $C_8$ | 5 | 43 | 53 | 61 | 67 | 79 | 82 | 95 |
| XXii-b | $C_8$ | 10 | 40 | 51 | 58 | 64 | 77 | 80 | 88 |
| XXii-c | $C_8$ | 15 | 37 | 47 | 53 | 62.5 | 75 | 78 | 86 |
| XXiii-a | $C_{10}$ | 5 | 41 | 52 | 58 | 65 | 76.5 | 79 | 87 |
| XXiii-b | $C_{10}$ | 10 | 40 | 49 | 56 | 64 | 73 | 76 | 84 |
| XXiii-c | $C_{10}$ | 15 | 36 | 45 | 53 | 61 | 72 | 74 | 83 |

**n = number of PO. units**

Table (23): **Biodegradability of oxypropenoxylated *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-octadec9-enamide sulfates:**

| Compound No. | R̀ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **XXIi-a** | $C_6$ | 5 | 40 | 48 | 60 | 67 | 76 | 79 | 90 |
| **XXIi-b** | $C_6$ | 10 | 38 | 47 | 58 | 64 | 71 | 77 | 83 |
| **XXIi-c** | $C_6$ | 15 | 39 | 43 | 55 | 63 | 70 | 76 | 80 |
| **XXIii-a** | $C_8$ | 5 | 38 | 46 | 57 | 63 | 70 | 73 | 83 |
| **XXIii-b** | $C_8$ | 10 | 36.5 | 43 | 55 | 62 | 69 | 71 | 80 |
| **XXIii-c** | $C_8$ | 15 | 34 | 42 | 54 | 59 | 65 | 70 | 76 |
| **XXIiii-a** | $C_{10}$ | 5 | 35 | 43 | 54 | 60 | 68 | 74 | 84 |
| **XXIiii-b** | $C_{10}$ | 10 | 33 | 42 | 53 | 58 | 67 | 69 | 80 |
| **XXIiii-c** | $C_{10}$ | 15 | 32.5 | 39.5 | 50 | 57 | 65 | 67 | 75 |

**n = number of PO. units**

Table (24) : ***Biodegradability of N,N*-bis(5-hydroxy-3,7-dioxa-alkyl)-alkenamide sulfates:**

| Compound No. | R | R̀ | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXIIi | $C_{12}$ | $C_6$ | 49 | 60 | 70 | 82 | 91 | - | - |
| XXIIi | $C_{12}$ | $C_8$ | 47 | 59 | 69 | 75 | 86 | 96 | - |
| XXIIi | $C_{12}$ | $C_{10}$ | 43 | 55 | 63 | 72 | 85 | 93 | - |
| XXIIIii | $C_{14}$ | $C_6$ | 48 | 64 | 73 | 79 | 84 | 94 | - |
| XXIIIii | $C_{14}$ | $C_8$ | 45 | 58 | 68 | 76 | 82 | 90 | - |
| XXIIIii | $C_{14}$ | $C_{10}$ | 41 | 52 | 64 | 71 | 81 | 89 | - |
| XXIViii | $C_{18}$ | $C_6$ | 39 | 52 | 61 | 73 | 79 | 88 | 94 |
| XXIViii | $C_{18}$ | $C_8$ | 38 | 49 | 58 | 72 | 78 | 84 | 93 |
| XXIViii | $C_{18}$ | $C_{10}$ | 34 | 45 | 56 | 67.5 | 72 | 80 | 89 |

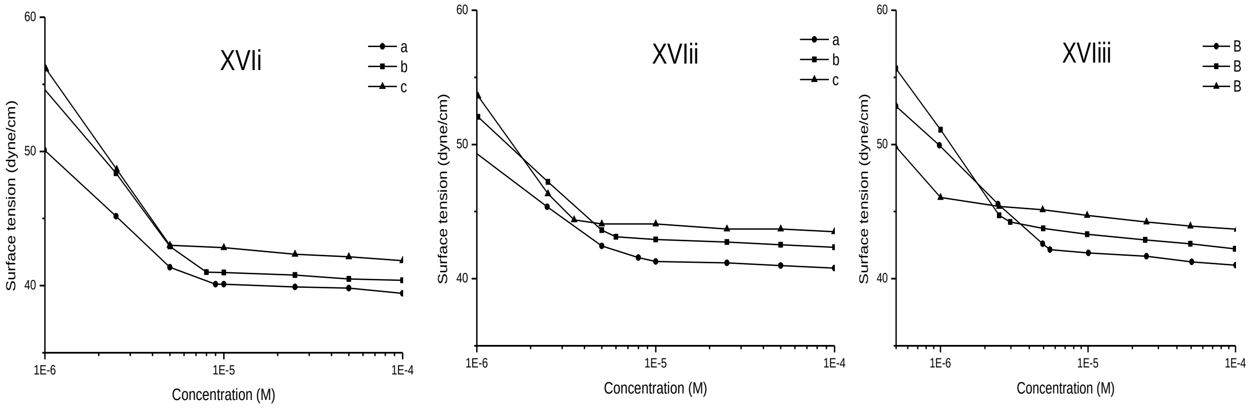


**Fig. 56: The plot of surface tension versus the logarithmic molar surfactant concentration of the (XVIi-iii)a-c.**

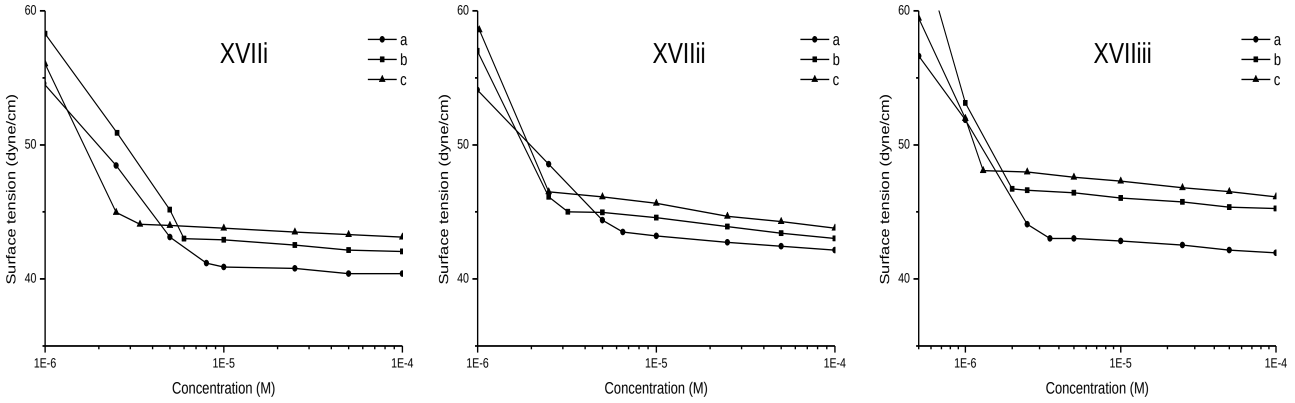


**Fig.57:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XVIIi-iii)a-c.**

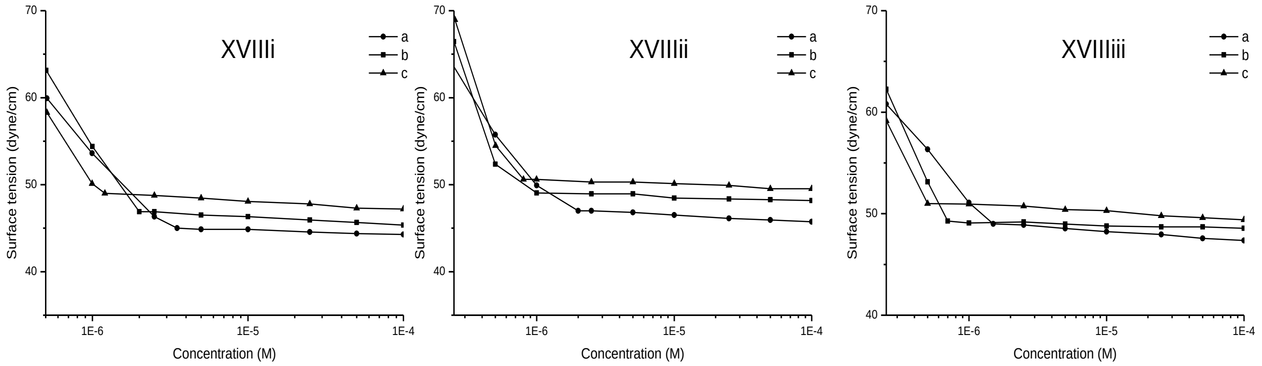


**Fig.58:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XVIIIi-iii)a-c.**

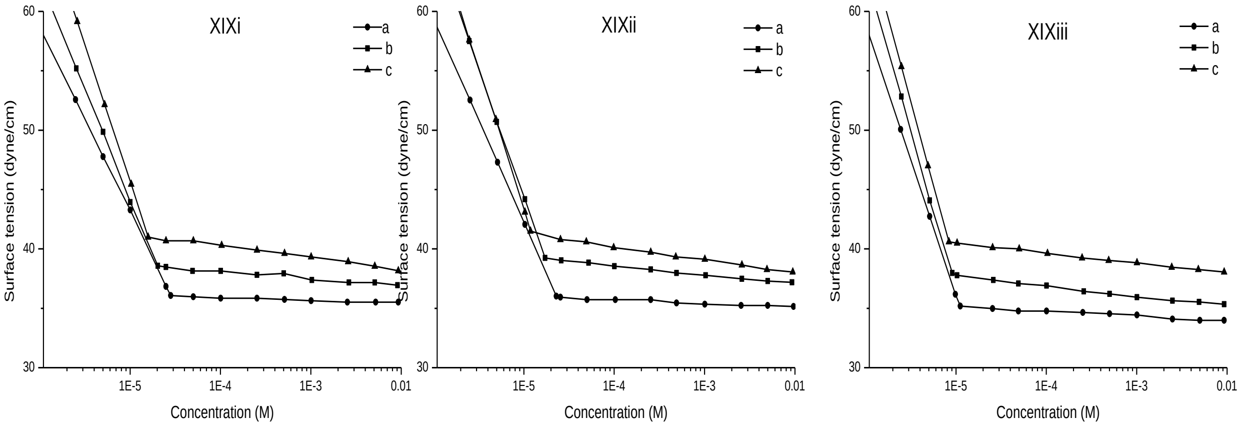


Fig. 59:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XIXi-iii)a-c.

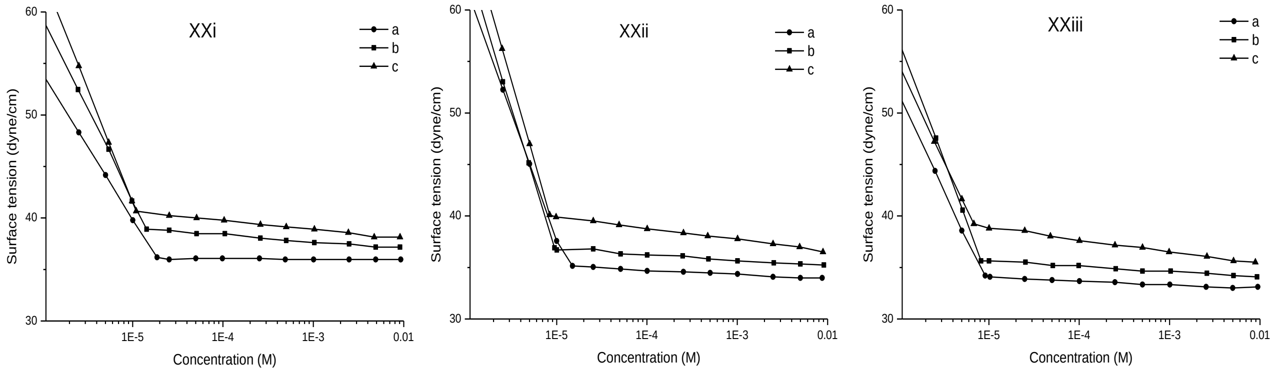


Fig. 60:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXi-iii)a-c.

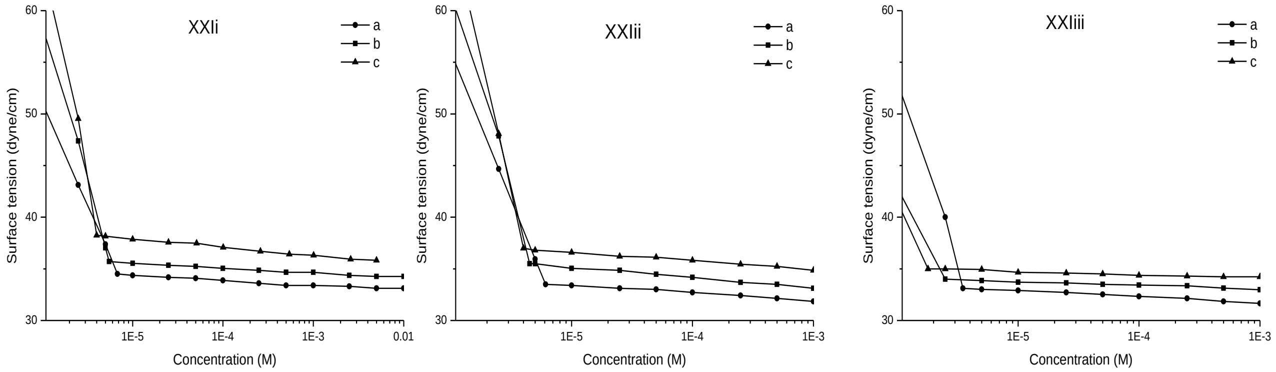


Fig. 61:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXIi-iii)a-c.

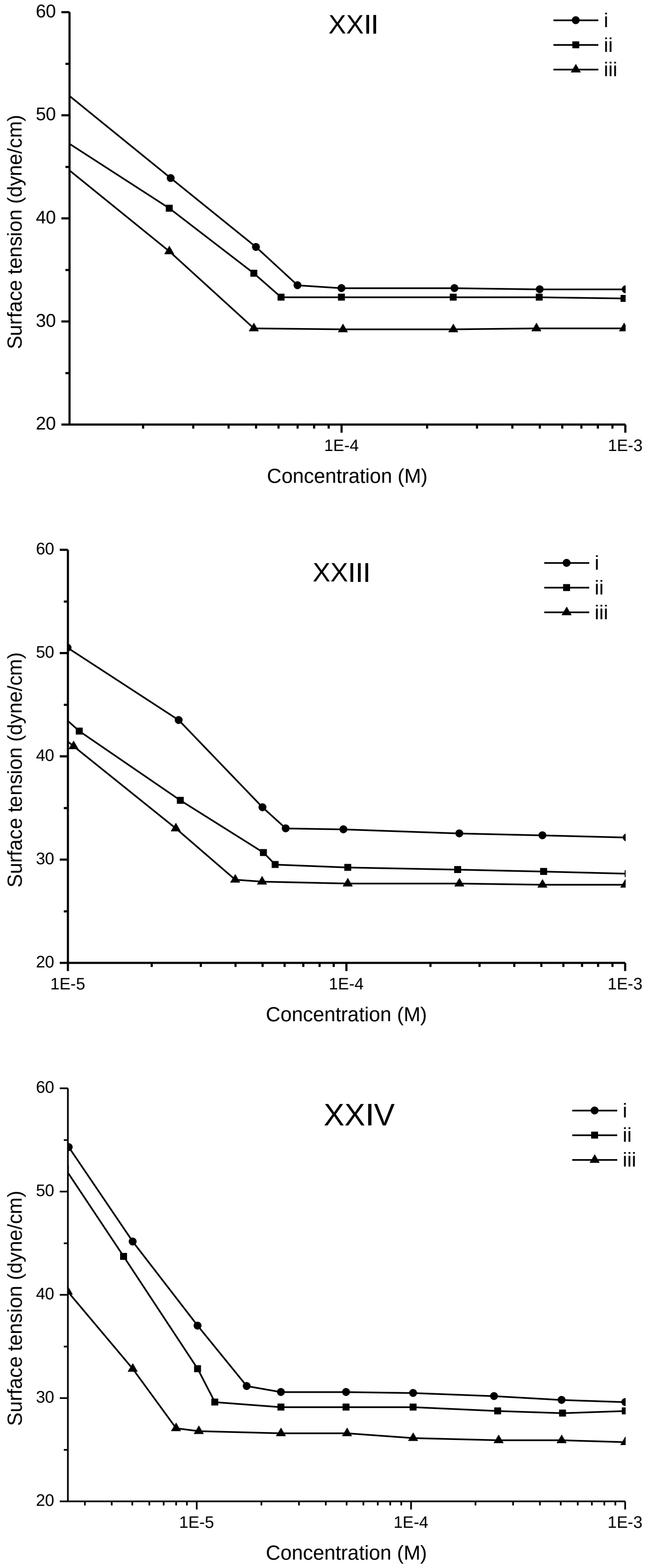


**Fig.62:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXII-XXIV)i-iii.**

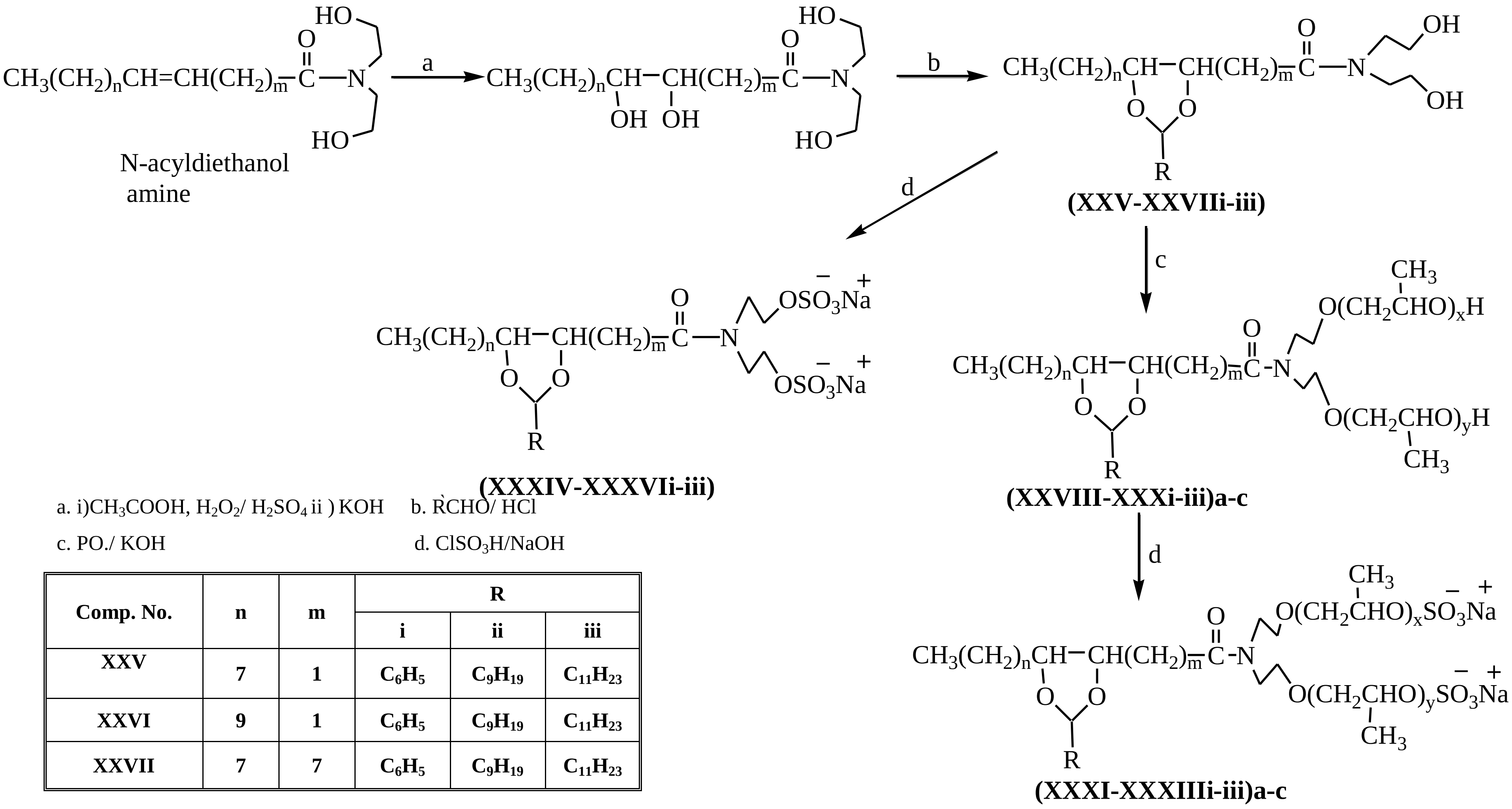
# *Part (III)*

## Synthesis and surface properties of gemini surfactants bearing 1,3-dioxolane ring:

There is an increasing interest in surfactants that contain a linkage that breaks down in a controlled way. The attitude toward easily cleavable surfactants has changed. Environmental concern has become one of the main driving forces for the development of new surfactants and rate of biodegradation has become a major issue.

The mechanism by which the cleavage occurs may vary and examples include acid hydrolysis, alkaline hydrolysis, UV irradiation, heat decomposition and enzymatic hydrolysis. The weak bond is usually positioned between the polar head group and the hydrophobic tail but there are also examples of surfactants with the sensitive linkage situated somewhere in the tail. Surfactants with a weak bond inserted into the structure are commonly called cleavable surfactants. Surfactants containing dioxolane ring are a very interested cleavable surfactants. They are typically synthesized from a long chain aldehyde by reaction with a vicinal diol or a higher polyol.

In this section we have synthesised a series of gemini surfactants (nonionic, anionic-nonioinc and anionic) bearing 1,3-dioxolane ring in their structure. The synthetic methods to prepare these compounds are outlined in (scheme 3), The surface active properties for these compounds were measured and discussed .



**(XXV-XXVIIi-iii)**

**(XXXIV-XXXVIi-iii)**

**(XXVIII-XXXi-iii)a-c**

**(XXXI-XXXIIIi-iii)a-c**

a. i)$CH_3COOH$, $H_2O_2$/ $H_2SO_4$ ii ) KOH b. RCHO/ HCl

c. PO./ KOH d. $ClSO_3H$/NaOH

| Comp. No. | n | m | R | | |
|---|---|---|---|---|---|
| | | | i | ii | iii |
| XXV | 7 | 1 | $C_6H_5$ | $C_9H_{19}$ | $C_{11}H_{23}$ |
| XXVI | 9 | 1 | $C_6H_5$ | $C_9H_{19}$ | $C_{11}H_{23}$ |
| XXVII | 7 | 7 | $C_6H_5$ | $C_9H_{19}$ | $C_{11}H_{23}$ |

**And x + y: a = 5 , b = 10 and c = 15 Mole of PO.**

**Scheme 3**

## *III.a-Preparation of vicinal dihydroxy fatty acid methyl ester:*

Refluxing fatty acid methyl ester with glacial acetic acid and hydrogen peroxide in the presence of sulphuric acid as a catalyst, followed by hydrolysis with potassium hydroxide in water – ethanol mixture afforded vicinal dihydroxy fatty acid methyl ester.

The structure of vicinal dihydroxy fatty acids methyl ester was confirmed via their IR, which revealed the presence of bands at 3363 $cm^{-1}$ corresponding to ν –OH and band at 1739 $cm^{-1}$ corresponding to ν –C=O of methyl ester (cf. Fig. 20)

## *III.b-Preparation of vicinal dihydroxy N-acyldiethanol-amine:*

Dihydroxy N-Acyldiethanolamine was prepared from the methyl ester of dihydroxy acids with diethanolamine in the presence of metallic sodium as mentioned before at part II.

## *III.c-Preparation of 1,3-dioxolane derivatives:*

The dihydroxy N-Acyldiethanolamine (3,4-dihydroxy N-dodecanyldiethanolamine, 3,4-dihydroxy N-tetradecanyldiethanolamine or 9,10-dihydroxy N-octadecanyldiethanol-amine) were refluxed with the aldehyde compound (benzaldehyde, decanal or dodecanal) in the presence of p-toluenesulfonic acid, give N,N-bis-(2-hydroxy-ethyl)-2-(2-(phenyl, nonyl or undecyl)-5-alkyl-[1,3]dioxolan-4-yl)-acetamide or octanamide (XXV-XXVIIi-iii). Table 25 shows the spectral data of N,N-bis-(2-hydroxy-ethyl)-2-(2-undecyl-5-octyl-[1,3]dioxolan-4-yl)-acetamide (XXViii), N,N-bis-(2-hydroxy-ethyl)-2-(2- phenyl-5-decyl-[1,3]dioxolan-4-yl)-acetamide (XXVIi) and N,N-bis-(2-hydroxy-ethyl)-8-(2-nonyl-5-octyl-[1,3]dioxolan-4-yl)-octanamide (XVIIii).

| Comp. | R | $^1$H-NMR (δ) | IR |
|---|---|---|---|
| XXViii | **$C_{11}H_{23}$** | 0.76 [t, 6H, terminal (-CH$_3$)], 1.18-1.46 [m, 34H, (-CH$_2$) of alkyl chain], 1.91 [s, 2H (-OH)], 2.17 [s, 2H, -CH$_2$-C=O], 3.20 [t, 4H,(-N-(CH$_2$)-], 3.76 [t, 4H, 2(-(CH$_2$)-OH)], 4.07-4.18 [m, 2H, (-O-CH-CH-O- of dioxolane ring], 4.76 [t, 1H, -O-CH-O- of dioxolane ring]. | 3425 cm$^{-1}$ (ν –OH), 2926, 2854 cm$^{-1}$ (ν –CH- aliphatic), 1639 cm$^{-1}$ (ν –C=O amide), 1465 cm$^{-1}$ (ν –CH$_3$ bending) and 1170, 1058 cm$^{-1}$ (ν –O– ether linkage) |
| XXVIi | **$C_6H_5$** | 0.82 [t, 6H, terminal (-CH$_3$)], 1.2-1.5 [m, 18H, (-CH$_2$) of alkyl chain], 2.03 [s, 2H (-OH)], 2.24 [s, 2H, -CH$_2$-C=O], 3.27 [t, 4H, (-N-(CH$_2$)-], 3.52 [t, 4H, 2(-(CH$_2$)-OH)], 3.96-4.19 [m, 2H, (-O-CH-CH-O-], 6.20 [s, 1H -O-CH-O- of dioxolane ring], 7.23-7.62 m, 5H, of phenyl group]. | 3404 cm$^{-1}$ (ν –OH), 3034 cm$^{-1}$ (ν =CH- aromatic), 2924, 2853 cm$^{-1}$ (ν –CH- aliphatic), 1639 cm$^{-1}$ (ν –C=O amide), 14636 cm$^{-1}$ (ν –CH$_3$ bending) and 11203,1069 cm$^{-1}$ (ν –O– ether linkage) |
| XXVIIii | **$C_9H_{17}$** | 0.76 [t, 6H, terminal (-CH$_3$)], 1.18-1.52 [m, 44H, (-CH$_2$) of alkyl chain], 2.07 [s, 2H (-OH)], 2.17 [s, 2H, -CH$_2$-C=O], 3.02 [t, 4H,(-N-(CH$_2$)-], 3.40 [t, 4H, 2(-(CH$_2$)-OH)], 4.00-4.19 [m, 2H, (-O-CH-CH-O- of dioxolane ring], 4.76 [t, 1H, -O-CH-O- of dioxolane ring]. | 3448 cm$^{-1}$ (ν –OH), 2923, 2851 cm$^{-1}$ (ν –CH- aliphatic), 1640 cm$^{-1}$ (ν –C=O amide), 1461 cm$^{-1}$ (ν –CH$_3$ bending) and 1169 cm$^{-1}$ (ν –O– ether linkage) |

**Table 25: spectral data of compounds XXViii, XXVIi and XXVIIii.**

Fig. 21-23 and fig.45-47 show the IR and $^1$HNMR spectra of these compounds.

Three types of Gemini surfactants were prepared from this compound :

## III.d- Nonionic gemini surfactants:

The nonionic gemini surfactants (XXVIII- XXXi-iii)a-c was obtained by the addition of different moles (n) of propylene oxide (n ~ 5,10 and 15). The structures of the synthesized these nonionic gemini surfactants were confirmed *via* IR and $^1$HNMR spectrum. IR of the compounds (XXIXii)a-c exhibit characteristic bands of the ether linkage of polypropenoxy chain (ν -C-O-C) at 1110-1114 cm$^{-1}$ and at 1640.2 cm$^{-1}$ characteristic for ν –C=O of amide (*cf.* fig. 24-26). The $^1$HNMR spectrum of XXIXi-a spectra showed that, the characteristic protons of propenoxy group at $\delta = 3.36$- 4.04 ppm (*cf.* Fig 48). The surface active properties of these surfactants were listed in (tables 27-29).

## III.e- Anionic- nonionic surfactants:

All the nonionic prepared surfactants converted to anionic ones by the sulfation followed by neutralization *via* sodium hydroxide, to give surfactants have both anionic and nonionic properties. Tables 30-32 showed the surface active properties of the compounds (XXXI- XXXIIIi-iii)a-c.

## III.f- Anionic surfactants:

The compounds (XXV-XXVIIi-iii) were sulfated with chlorosulfonic acid and then neutralized by sodium hydroxide, obtained an anionic gemini surfactants (XXXIV- XXXVIi-iii). The IR spectrum of (XXXVii) shows that, bands at 1130 cm$^{-1}$ characteristic for (ν -$SO_2$), 1636 cm$^{-1}$ characteristic for ν –C=O of amide and the disappearance of ν –OH band (*cf.*

fig. 27). Also it indicated by elemental analysis which listed in (table 26). The surface active properties of these surfactants were listed in (table 33).

## *Surface active properties and related properties:*

The surface activity and related properties of the synthesized 1,3-dioxolane derivatives (XXVIII-XXXi-iii)a-c, (XXXI-XXXIIIi-iii)a-c and (XXXIV-XXXVI)i-iii, including , surface and interfacial tension, kraft point, wetting time, foam height, emulsion stability, and cloud point for nonionic Gemini surfactants are given in (tables 27-33).

### 1- Surface and Interfacial tensions :

The surface and interfacial tension of 1,3-dioxolane derivatives showed lower values than triple chain gemini surfactants. Compounds (XXXIV-XXXVI)i-iii anionic one in (table 33) reported, lower values for surface and interfacial tension than the other two types of gemini surfactants [(XXVIII-XXXi-iii)a-c, (XXXI-XXXIIIi-iii)a-c]. Moreover, its surface tension decreases with increasing the alkyl chain length. Also, the surface and interfacial tension for [(XXVIII-XXXi-iii)a-c, (XXXI-XXXIIIi-iii)a-c] increase with increasing the polypropenoxy chain adduct in the molecule of surfactant.

On the other hand, synthesized surfactants which include a phenyl group into their structure show higher values of surface and interfacial tension between all the prepared surfactants.

### 2- Kraft point :

The Kraft point for the anionic 1,3-dioxolane derivatives or anionic-nonionic (XXXIV-XXXVI)i-iii, (XXXI-XXXIIIi-iii)a-c is $< 0^{o}$C, all the synthesized surfactants are freely soluble in water at 1 wt% concentration.

### 3-Cloud point:

The nonionic gemini surfactants (XXVIII-XXXi-iii)a-c have higher cloud point, where the propenoxylated *N*,*N*-bis-(2-hydroxyethyl)-2-(2-nonyl-5-

octyl-[1,3]dioxolan-4-yl)acetamide (XXVIIIi-iii)a-c recorded highest cloud points ( 55- 70$^{o}$C). As expected, as the percentage of propylene oxide units increased in the surfactants molecule the cloud point increased too (tables 27-29).

## 3- Wetting time :

All the synthesized surfactants have a good wetting time. The compounds (XXXi-iii)a-c show a higher wetting time compared with other synthesized surfactants. On the other hand, the anionic-nonionic Gemini surfactants (XXXI-XXXIIIi-iii)a-c show the lower wetting time among all the prepared surfactants, while the introduction of propylene oxide groups between the hydrophilic (-$SO_4$Na) and hydrophobic (R) groups in the surfactant molecule unfavourable to wetting power, while the wetting time increase with the introduction of each additional propylene oxide unit(203).

## 4- Emulsifying properties :

The gemini nonionic surfactants (XXVIII-XXXi-iii)a-c , containing 1,3-dioxolane ring possess good emulsifying properties than the corresponding anionic surfactants containing 1,3- dioxolane ring [(XXXI-XXXIIIi-iii)a-c and (XXXIV-XXXVI)i-iii] respectively. Moreover, anionic gemini surfactants (XXXIV-XXXVI)i-iii recorded lower emulsifying properties (tables 33).

All prepared surfactants bearing a phenyl group in its structure show lower emulsification power than other corresponding surfactants.

## 5- Foaming power :

From the data listed in (tables 27-33) for the foam height it revealed that, the foam height increase with increasing the alkyl chain length. As expected the nonionic gemini surfactants (XXVIII-XXXi-iii)a-c have the lower values of foam height, while the anionic one (XXXIV-XXXVI)i-iii has the highest foam. On the other hand, the compounds (XXXI-XXXIIIi-iii)a-c which propylene oxide units into their structure, exhibit decreasing in the foam height with increasing the propylene oxide unit in surfactant molecule.

## 6- Critical micelle concentration (CMC) :

The values of *CMC* and the surface tension at *CMC* are listed in (tables 45-51), firstly we can obtained that, the nonionic gemini surfactants (XXVIII-XXXi-iii)a-c have the lower values of *CMC* (tables 27-29). And as expected, the anionic gemini compounds (XXXIV-XXXVI)i-iii exhibit a *CMC* value higher than that of the other two types (table 33) that due to stronger repulsive electrostatic nature of the polar group.(cf. Fig. 63- 69).

## 7- Biodegradability :

The biodegradation of the 1,3-dioxolane derivatives gave satisfactory results. All the examined surfactants bearing 1,3-dioxolane ring had a much higher rate of degradation. This may be attributed to easily hydrolyzed of 1,3-dioxolane ring especially under acidic condition. Furthermore the gemini anionic surfactants are more biodegradable than the other two types of surfactants bearing 1,3-dioxolane ring.

Also the biodegradability decreases as the number of propylene oxide units increased in the surfactant molecules (cf. tables 34-40).

Table(26):**Elemental analysis of *N,N*-bis-(2-hydroxy-ethyl)- (2, 5-dialkyl-[1,3]dioxolan-4-yl)-alkanamide:**

| Comp. No. | M. Formula | M. Wt. | C% | | H% | | N% | | S% | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| XXXIVi | $C_{23}H_{35}NO_{11}S_2Na_2$ | 611.14 | 45.17 | 44.68 | 5.77 | 5.42 | 2.29 | 2.01 | 10.49 | 10.11 |
| XXXIVii | $C_{26}H_{49}NO_{11}S_2Na_2$ | 661.78 | 47.19 | 46.87 | 7.46 | 7.09 | 2.12 | 1.92 | 9.69 | 9.54 |
| XXXIViii | $C_{28}H_{53}NO_{11}S_2Na_2$ | 689.83 | 48.75 | 48.25 | 7.74 | 7.15 | 2.03 | 1.90 | 9.30 | 9.19 |
| XXXVi | $C_{25}H_{39}NO_{11}S_2Na_2$ | 639.69 | 46.94 | 46.58 | 6.15 | 5.87 | 2.19 | 1.99 | 10.03 | 9.75 |
| XXXVii | $C_{28}H_{53}NO_{11}S_2Na_2$ | 689.83 | 48.75 | 48.31 | 7.74 | 7.25 | 2.03 | 1.87 | 9.30 | 9.11 |
| XXXViii | $C_{30}H_{57}NO_{11}S_2Na_2$ | 717.32 | 50.19 | 49.76 | 8.00 | 7.67 | 1.95 | 1.62 | 8.93 | 8.65 |
| XXXVIi | $C_{29}H_{47}NO_{11}S_2Na_2$ | 695.80 | 50.06 | 49.73 | 6.81 | 6.37 | 2.01 | 1.84 | 9.22 | 8.97 |
| XXXVIii | $C_{32}H_{61}NO_{11}S_2Na_2$ | 745.94 | 51.52 | 51.12 | 8.24 | 7.97 | 1.88 | 1.49 | 8.60 | 8.45 |
| XXXVIiii | $C_{34}H_{65}NO_{11}S_2Na_2$ | 773.99 | 52.76 | 52.37 | 8.46 | 8.14 | 1.81 | 1.42 | 8.29 | 7.91 |

Table(27): **Surface properties of oxypropenoxylated *N,N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-acetamide:**

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) 10$^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXVIIIi-a | Ph | 5 | 40 | 11 | 47 | 43 | 63 | 55 | 6.5 | 41 |
| XXVIIIi-b | Ph | 10 | 41 | 12.5 | 56 | 65 | 49 | 60 | 5.4 | 43 |
| XXVIIIi-c | Ph | 15 | 42.5 | 13.5 | 61 | 90 | 41 | 70 | 4.3 | 45 |
| XXVIIIii-a | $C_9$ | 5 | 37.5 | 9 | 55 | 63 | 78 | 50 | 2.1 | 39 |
| XXVIIIii-b | $C_9$ | 10 | 39.5 | 10.5 | 60 | 59 | 63 | 65 | 1.8 | 41.5 |
| XXVIIIii-c | $C_9$ | 15 | 41.5 | 11 | 70 | 85 | 51 | 75 | 1.5 | 43 |
| XXVIIIiii-a | $C_{11}$ | 5 | 38.5 | 10.5 | 51 | 85 | 82 | 60 | 2.0 | 40 |
| XXVIIIiii-b | $C_{11}$ | 10 | 40 | 12 | 66 | 95 | 69 | 75 | 1.5 | 42.5 |
| XXVIIIiii-c | $C_{11}$ | 15 | 42 | 13 | 65 | 98 | 62 | 80 | 0.9 | 44 |

**n = number of PO. units**

Table(28): **Surface properties of oxypropenoxylated *N,N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-decyl-[1,3]dioxolan-4-yl)-acetamide:**

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXIXi-a | Ph | 5 | 41.5 | 12 | 44 | 50 | 57 | 60 | 6.0 | 42 |
| XXIXi-b | Ph | 10 | 42.5 | 13 | 49 | 58 | 52 | 60 | 4.4 | 44 |
| XXIXi-c | Ph | 15 | 43 | 14.5 | 58 | 60 | 39 | 70 | 4.0 | 45 |
| XXIXii-a | $C_9$ | 5 | 39 | 11 | 49 | 75 | 78 | 65 | 1.5 | 41 |
| XXIXii-b | $C_9$ | 10 | 41 | 12.5 | 52 | 62 | 63 | 70 | 1.1 | 42.5 |
| XXIXii-c | $C_9$ | 15 | 42 | 13 | 69 | 73 | 57 | 85 | 0.8 | 44 |
| XXIXiii-a | $C_{11}$ | 5 | 41 | 12 | 44 | 78 | 81 | 55 | 1.0 | 41.5 |
| XXIXiii-b | $C_{11}$ | 10 | 42 | 13 | 52 | 82 | 76 | 80 | 0.8 | 43 |
| XXIXiii-c | $C_{11}$ | 15 | 43.5 | 14.5 | 57 | 86 | 71 | 90 | 0.7 | 45 |

**n = number of PO. units**

Table (29) : **Surface properties of oxypropenoxylated *N*,*N*-bis-(2-hydroxy-ethyl)-8-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-octanamide:**

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXi-a | Ph | 5 | 43 | 11 | 34 | 75 | 66 | 40 | 3.5 | 44 |
| XXXi-b | Ph | 10 | 44.5 | 13 | 38 | 90 | 61 | 45 | 2.3 | 46.5 |
| XXXi-c | Ph | 15 | 45.5 | 14.5 | 43 | 110 | 55 | 45 | 1.5 | 47.5 |
| XXXii-a | $C_9$ | 5 | 42.5 | 12 | 36 | 118 | 91 | 40 | 0.7 | 44 |
| XXXii-b | $C_9$ | 10 | 43 | 13 | 43 | 100 | 80 | 40 | 0.65 | 45 |
| XXXii-c | $C_9$ | 15 | 44 | 15 | 53 | 115 | 70 | 50 | 0.45 | 46.5 |
| XXXiii-a | $C_{11}$ | 5 | 43 | 14 | 35 | 130 | 96 | 45 | 0.54 | 44 |
| XXXiii-b | $C_{11}$ | 10 | 45 | 12.5 | 42 | 140 | 94 | 50 | 0.32 | 46.5 |
| XXXiii-c | $C_{11}$ | 15 | 46.5 | 14 | 51 | 163 | 83 | 65 | 0.28 | 48.5 |

**n = number of PO. units**

Table (30) : **Surface properties of oxypropenoxylated *N,N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-acetamide sulfates:**

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXIi-a | Ph | 5 | 37 | 12 | < 0 | 39 | 3 : 30 | 120 | 8.4 | 38.5 |
| XXXIi-b | Ph | 10 | 39.5 | 12.5 | < 0 | 42 | 3 : 23 | 110 | 7.5 | 41 |
| XXXIi-c | Ph | 15 | 40.5 | 13 | < 0 | 48 | 3 : 14 | 90 | 6.3 | 42.5 |
| XXXIii-a | $C_9$ | 5 | 36.5 | 11 | < 0 | 45 | 5 : 50 | 150 | 3.1 | 37.5 |
| XXXIii-b | $C_9$ | 10 | 38 | 12 | < 0 | 48 | 5 : 31 | 130 | 2.5 | 39.5 |
| XXXIii-c | $C_9$ | 15 | 38.5 | 13 | < 0 | 51 | 5 : 20 | 120 | 1.5 | 43 |
| XXXIiii-a | $C_{11}$ | 5 | 35 | 10.5 | < 0 | 47 | 6 : 10 | 150 | 2.8 | 37 |
| XXXIiii-b | $C_{11}$ | 10 | 36.5 | 12 | < 0 | 50 | 6 : 02 | 135 | 1.9 | 38.5 |
| XXXIiii-c | $C_{11}$ | 15 | 38 | 15.2 | < 0 | 51 | 5 : 51 | 130 | 1.3 | 41.5 |

**n = number of PO. units**

Table (31): **Surface properties of oxypropenoxylated *N,N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-decyl-[1,3]dioxolan-4-yl)-acetamide sulfates:**

| Compound No. | R | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| **XXXIIi-a** | Ph | **5** | **37.5** | **12** | **< 0** | **42** | **4 : 00** | **130** | **8.0** | **38** |
| **XXXIIi-b** | Ph | **10** | **38.5** | **12.5** | **< 0** | **49** | **3 : 39** | **110** | **6.4** | **40** |
| **XXXIIi-c** | Ph | **15** | **40** | **13** | **< 0** | **52** | **3 : 01** | **100** | **5.8** | **42** |
| **XXXIIii-a** | $C_9$ | **5** | **35** | **11** | **< 0** | **51** | **6 : 00** | **150** | **3.7** | **36** |
| **XXXIIii-b** | $C_9$ | **10** | **37** | **11** | **< 0** | **54** | **5 : 43** | **140** | **1.3** | **39.5** |
| **XXXIIii-c** | $C_9$ | **15** | **37.5** | **12** | **< 0** | **60** | **5 : 20** | **130** | **0.92** | **44** |
| **XXXIIiii-a** | $C_{11}$ | **5** | **34** | **9** | **< 0** | **52** | **6 : 30** | **160** | **1.2** | **35** |
| **XXXIIiii-b** | $C_{11}$ | **10** | **36** | **11** | **< 0** | **57** | **6 : 14** | **150** | **1.0** | **38** |
| **XXXIIiii-c** | $C_{11}$ | **15** | **37** | **11.5** | **< 0** | **63** | **6 : 10** | **135** | **0.80** | **40** |

**n = number of PO. units**

Table (32): **Surface properties of *N*,*N*-bis-(2-hydroxy-ethyl)-8-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-octanamide sulfates:**

| **Compound No.** | **R** | **n** | **Surface tension (dyne/cm) 0.1 %** | **Interfacial tension (dyne/cm) 0.1 %** | **Kraft Point °C 1.0 %** | **Wetting time (Second) 1.0 %** | **Emulsion stability (min : Sec.) 1.0 %** | **Foam height (mm) 1.0 %** | CMC (M) **$10^{-4}$** | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| **XXXIIIi-a** | Ph | **5** | **36** | **11** | **< 0** | **45** | **5 : 51** | **140** | **3.9** | **36** |
| **XXXIIIi-b** | Ph | **10** | **37** | **12** | **< 0** | **48** | **5 : 36** | **120** | **2.8** | **37.5** |
| **XXXIIIi-c** | Ph | **15** | **37.5** | **12.5** | **< 0** | **52** | **5 : 00** | **100** | **1.7** | **39.5** |
| **XXXIIIii-a** | $C_9$ | **5** | **34** | **10** | **< 0** | **55** | **7 : 00** | **175** | **0.80** | **35** |
| **XXXIIIii-b** | $C_9$ | **10** | **34.5** | **11** | **< 0** | **60** | **6 : 47** | **160** | **0.73** | **36.5** |
| **XXXIIIii-c** | $C_9$ | **15** | **36** | **12.5** | **< 0** | **60** | **6 : 28** | **130** | **0.54** | **37.5** |
| **XXXIIIiii-a** | $C_{11}$ | **5** | **32** | **10** | **< 0** | **56** | **7 : 30** | **190** | **0.65** | **33** |
| **XXXIIIiii-b** | $C_{11}$ | **10** | **33** | **10.5** | **< 0** | **64** | **7 : 21** | **180** | **0.52** | **34.5** |
| **XXXIIIiii-c** | $C_{11}$ | **15** | **35** | **12** | **< 0** | **70** | **7 : 03** | **160** | **0.39** | **39** |

**n = number of PO. units**

Table (33): **Surface properties of *N,N*-bis-(2-hydroxy-ethyl)- (2,5-dialkyl-[1,3]dioxolan-4-yl)-alkanamide sulfates:**

| Compound No. | R | R̀ | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXIVi | $C_{12}$ | Ph | 34.5 | 9.5 | < 0 | 69 | 2 : 20 | 180 | 10 | 36 |
| XXXIVii | $C_{12}$ | $C_9$ | 34 | 10.5 | < 0 | 76 | 2 : 50 | 200 | 4.5 | 35.5 |
| XXXIViii | $C_{12}$ | $C_{11}$ | 32 | 12 | < 0 | 86 | 2 : 55 | 150 | 3.2 | 33 |
| XXXVi | $C_{14}$ | Ph | 32 | 7 | < 0 | 71 | 3 : 20 | 190 | 9.2 | 33.5 |
| XXXVii | $C_{14}$ | $C_9$ | 31.5 | 10 | < 0 | 78 | 3 : 30 | 210 | 3.4 | 31.5 |
| XXXViii | $C_{14}$ | $C_{11}$ | 30 | 9 | < 0 | 81 | 4 : 30 | 220 | 1.5 | 30.5 |
| XXXVIi | $C_{18}$ | Ph | 30.5 | 9 | < 0 | 69 | 4 : 10 | 230 | 4.5 | 32 |
| XXXVIii | $C_{18}$ | $C_9$ | 30 | 12 | < 0 | 74 | 4 : 35 | 250 | 0.74 | 29.5 |
| XXXVIiii | $C_{18}$ | $C_{11}$ | 27 | 11 | < 0 | 89 | 5 : 20 | 260 | 0.59 | 27.5 |

Table (34): **Biodegradability of oxypropenoxylated *N,N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-acetamide:**

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **XXVIIIi-a** | Ph | **5** | 55 | 60 | 73.5 | 82 | 92 | - | - |
| **XXVIIIi-b** | Ph | **10** | 57 | 63 | 70 | 79 | 84 | 92 | - |
| **XXVIIIi-c** | Ph | **15** | 52 | 59 | 68 | 73.5 | 82 | 90 | 96 |
| **XXVIIIii-a** | $C_9$ | **5** | 56 | 68 | 72 | 81 | 86 | 95 | - |
| **XXVIIIii-b** | $C_9$ | **10** | 53 | 62 | 69 | 79 | 82 | 94 | - |
| **XXVIIIii-c** | $C_9$ | **15** | 51 | 60 | 71 | 76 | 80 | 91 | 95 |
| **XXVIIIiii-a** | $C_{11}$ | **5** | 49 | 58 | 68 | 77 | 81 | 92 | - |
| **XXVIIIiii-b** | $C_{11}$ | **10** | 48 | 55 | 64 | 72 | 80 | 89 | 96 |
| **XXVIIIiii-c** | $C_{11}$ | **15** | 41 | 52 | 63 | 69 | 76 | 86 | 94 |

**n = number of PO. units**

Table (35) : **Biodegradability of oxypropenoxylated *N*,*N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-decyl-[1,3]dioxolan-4-yl)-acetamide:**

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **XXIXi-a** | Ph | **5** | 50 | 63 | 71 | 79 | 86 | 98 | - |
| **XXIXi-b** | Ph | **10** | 48 | 59 | 69 | 75 | 82 | 93 | - |
| **XXIXi-c** | Ph | **15** | 46 | 57 | 61 | 71 | 84 | 92 | - |
| **XXIXii-a** | $C_9$ | **5** | 53 | 62 | 72 | 81 | 92 | - | - |
| **XXIXii-b** | $C_9$ | **10** | 52 | 60 | 67 | 74 | 81 | 90 | - |
| **XXIXii-c** | $C_9$ | **15** | 49 | 59 | 63 | 72 | 79 | 89 | 92 |
| **XXIXiii-a** | $C_{11}$ | **5** | 51 | 61 | 70 | 79 | 89 | 93 | - |
| **XXIXiii-b** | $C_{11}$ | **10** | 49 | 58 | 65 | 71 | 79 | 89 | 96 |
| **XXIXiii-c** | $C_{11}$ | **15** | 46 | 53 | 59 | 68 | 74 | 88 | 91 |

**n = number of PO. units**

Table (36) : **Biodegradability of oxypropenoxylated *N*,*N*-bis-(2-hydroxy-ethyl)-8-(2-alkyl-5octyl-[1,3]dioxolan-4-yl)-octanamide:**

| **Compound No.** | **R** | **n** | **1st day** | **2nd day** | **3rd day** | **4th day** | **5th day** | **6th day** | **7th day** |
|---|---|---|---|---|---|---|---|---|---|
| **XXXi-a** | Ph | **5** | 48 | 58 | 69 | 77 | 85 | 90 | - |
| **XXXi-b** | Ph | **10** | 46 | 55 | 64 | 74 | 81 | 86 | 93 |
| **XVIIIi-c** | Ph | **15** | 43 | 51.5 | 59 | 68 | 76 | 82 | 89 |
| **XXXii-a** | $C_9$ | **5** | 50 | 61 | 68 | 75 | 85 | 92 | 96 |
| **XXXii-b** | $C_9$ | **10** | 48 | 59 | 66 | 77 | 81 | 88 | 93 |
| **XXXii-c** | $C_9$ | **15** | 45 | 53 | 63 | 71 | 79 | 75 | 90 |
| **XXXiii-a** | $C_{11}$ | **5** | 47 | 59 | 64 | 72 | 84 | 88 | 92 |
| **XXXiii-b** | $C_{11}$ | **10** | 45 | 55 | 61 | 71 | 78 | 81 | 89 |
| **XXXiii-c** | $C_{11}$ | **15** | 41 | 52 | 59 | 69 | 72 | 79 | 84 |

**n = number of PO. units**

Table (37) : **Biodegradability of oxypropenoxylated *N,N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-acetamide sulfates:**

| **Compound No.** | **R** | **n** | **1st day** | **2nd day** | **3rd day** | **4th day** | **5th day** | **6th day** | **7th day** |
|---|---|---|---|---|---|---|---|---|---|
| **XXXIi-a** | Ph | **5** | 61 | 71 | 79.5 | 88 | 94 | - | - |
| **XXXIi-b** | Ph | **10** | 59 | 68 | 77 | 84 | 91 | 98 | - |
| **XXXIi-c** | Ph | **15** | 55 | 65 | 73 | 81 | 89 | 96 | - |
| **XXXIii-a** | $C_9$ | **5** | 64.5 | 76 | 84 | 87 | 95 | - | - |
| **XXXIii-b** | $C_9$ | **10** | 60 | 72 | 79 | 83 | 93 | 97 | - |
| **XXXIii-c** | $C_9$ | **15** | 59 | 68 | 74 | 79 | 87 | 94 | - |
| **XXXIiii-a** | $C_{11}$ | **5** | 93 | 73 | 80 | 85 | 93 | - | - |
| **XXXIiii-b** | $C_{11}$ | **10** | 59.5 | 69 | 76 | 81 | 87 | 91 | - |
| **XXXIiii-c** | $C_{11}$ | **15** | 51 | 59 | 64 | 76 | 82 | 88 | 94 |

**n = number of PO. units**

Table (38): **Biodegradability of oxypropenoxylated *N*,*N*-bis-(2-hydroxy-ethyl)-2-(2-alkyl-5-decyl-[1,3]dioxolan-4-yl)-acetamide sulfates:**

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **XXXIIi-a** | Ph | **5** | 58 | 68 | 77 | 84 | 91 | - | - |
| **XXXIIi-b** | Ph | **10** | 57 | 67 | 73 | 81 | 89 | 96 | - |
| **XXXIIi-c** | Ph | **15** | 53 | 64 | 71 | 76 | 88 | 94 | - |
| **XXXIIii-a** | $C_9$ | **5** | 60 | 72 | 80 | 87 | 93 | 97 | - |
| **XXXIIii-b** | $C_9$ | **10** | 59 | 69 | 74 | 82 | 88 | 93 | - |
| **XXXIIii-c** | $C_9$ | **15** | 53 | 65 | 71 | 78 | 84 | 90 | 97 |
| **XXXIIiii-a** | $C_{11}$ | **5** | 58 | 69 | 79 | 85 | 91 | - | - |
| **XXXIIiii-b** | $C_{11}$ | **10** | 54 | 64 | 75 | 71 | 87 | 90 | - |
| **XXXIIiii-c** | $C_{11}$ | **15** | 51 | 60 | 69 | 76 | 82 | 89 | 95 |

**n = number of PO. units**

Table (39) : **Biodegradability of oxypropenoxylated *N*,*N*-bis-(2-hydroxy-ethyl)-8-(2-alkyl-5-octyl-[1,3]dioxolan-4-yl)-octanamide sulfates:**

| Compound No. | R | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXIIIi-a | Ph | 5 | 53 | 64 | 72 | 80 | 88 | 92 | - |
| XXXIIIi-b | Ph | 10 | 51 | 62 | 71 | 79 | 84 | 90 | - |
| XXXIIIi-c | Ph | 15 | 48 | 59 | 67 | 74 | 82 | 86 | 94 |
| XXXIIIii-a | $C_9$ | 5 | 57 | 68 | 76 | 84 | 89 | 90 | 98 |
| XXXIIIii-b | $C_9$ | 10 | 55 | 65 | 73 | 81 | 86 | 91 | 93 |
| XXXIIIii-c | $C_9$ | 15 | 49 | 61 | 69 | 78 | 86 | 89 | 95 |
| XXXIIIiii-a | $C_{11}$ | 5 | 56 | 64 | 73 | 80 | 84 | 93 | - |
| XXXIIIiii-b | $C_{11}$ | 10 | 53 | 61 | 70 | 75 | 82 | 86 | 92 |
| XXXIIIiii-c | $C_{11}$ | 15 | 45 | 55 | 63 | 71 | 77 | 83 | 89 |

**n = number of PO. units**

Table (40) : **Biodegradability of *N,N*-bis-(2-hydroxy-ethyl)- (2,5-dialkyl-[1,3]dioxolan-4-yl)-alkanamide sulfates:**

| Compound No. | R | Ȓ | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| **XXXIVi** | $C_{12}$ | Ph | 65 | 76 | 84 | 93 | - | - | - |
| **XXXIVii** | $C_{12}$ | $C_9$ | 59 | 68 | 79 | 89 | 97 | - | - |
| **XXXIViii** | $C_{12}$ | $C_{11}$ | 56 | 63 | 73 | 82 | 94 | - | - |
| **XXXVi** | $C_{14}$ | Ph | 61 | 73 | 81 | 90 | 98 | - | - |
| **XXXVii** | $C_{14}$ | $C_9$ | 60 | 69 | 75 | 82 | 93 | - | - |
| **XXXViii** | $C_{14}$ | $C_{11}$ | 53 | 61 | 72 | 89 | 91 | 96 | - |
| **XXXVIi** | $C_{18}$ | Ph | 54 | 67 | 73 | 84 | 93 | 98 | - |
| **XXXVIii** | $C_{18}$ | $C_9$ | 56 | 65 | 71 | 77 | 84 | 90 | 96 |
| **XXXVIiii** | $C_{18}$ | $C_{11}$ | 48 | 69 | 68 | 72 | 80 | 87 | 92 |

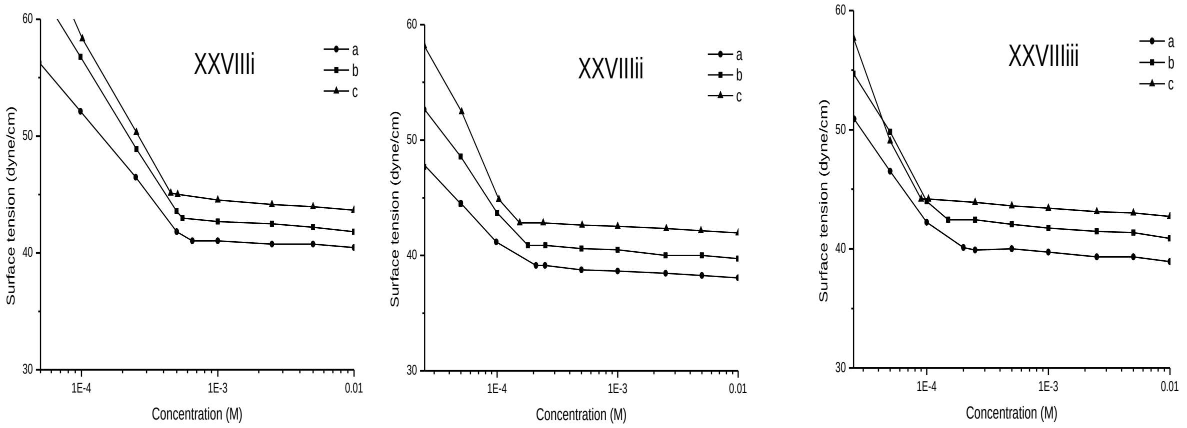


Fig.63:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXVIIIi-iii)a-c.

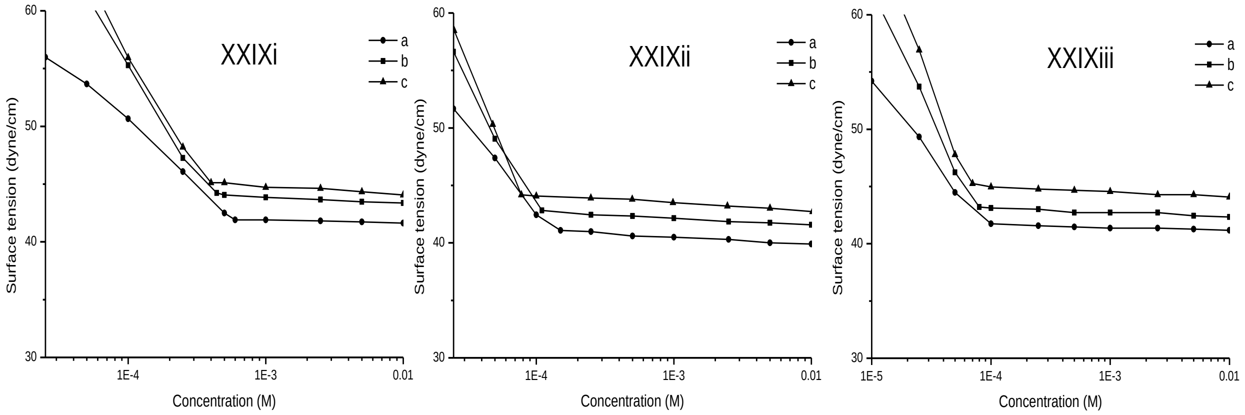


Fig.64:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXIXi-iii)a-c.

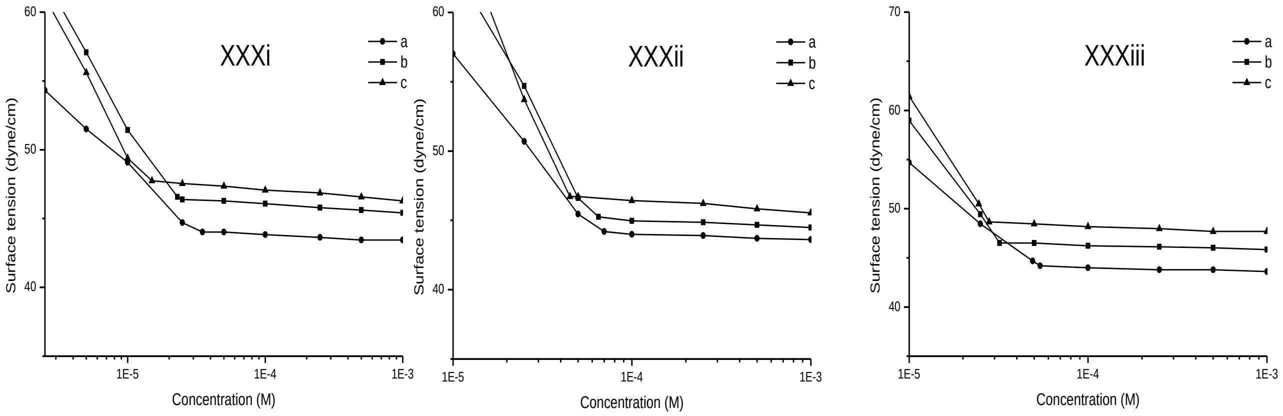


Fig.65:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXi-iii)a-c.

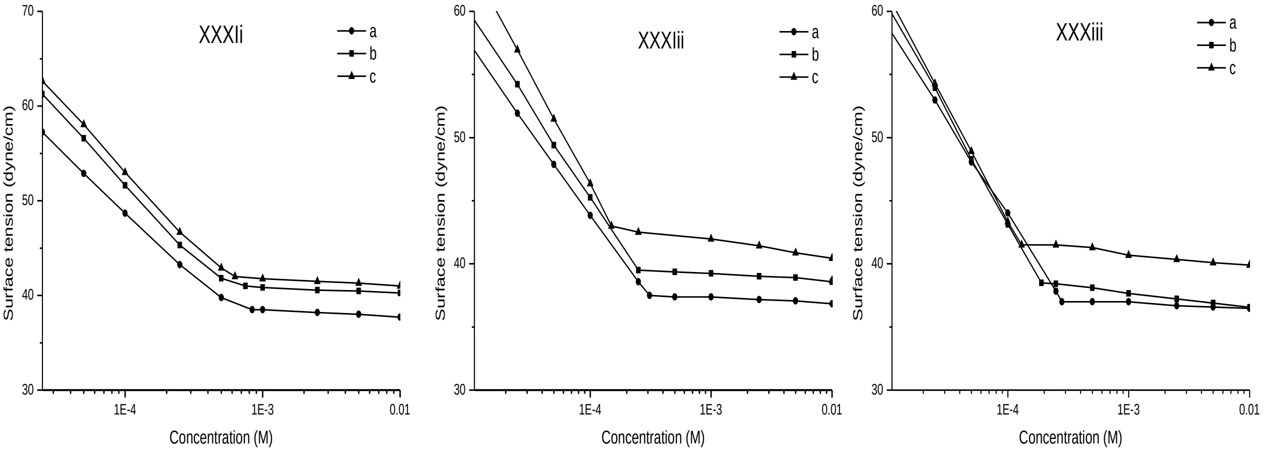


**Fig. 66:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXIi-iii)a-c.**

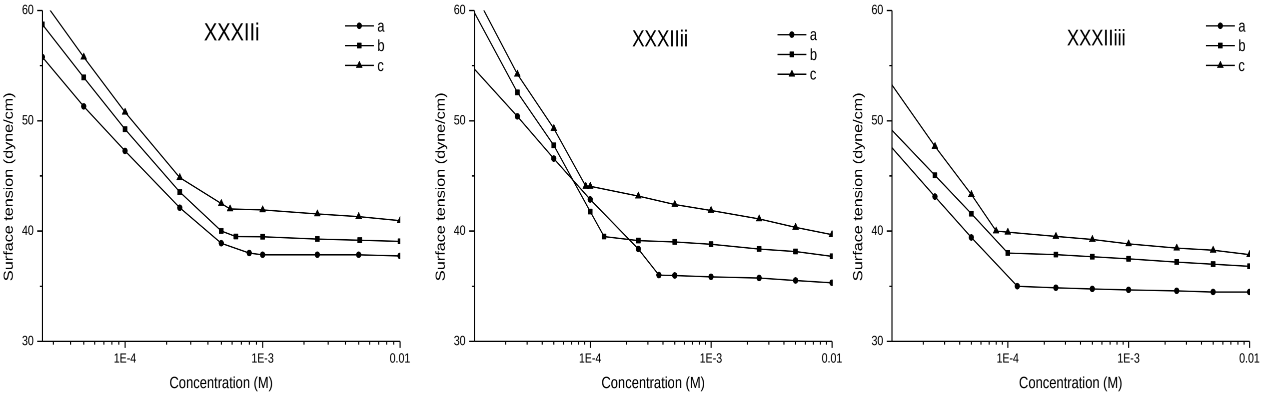


**Fig. 67:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXIIi-iii)a-c.**

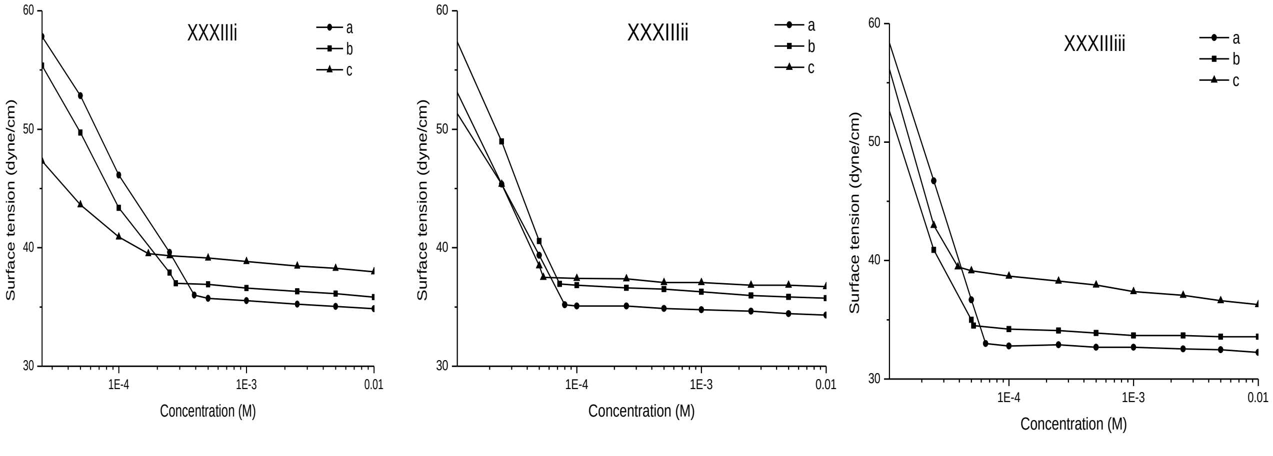


**Fig. 68:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXIIIi-iii)a-c.**

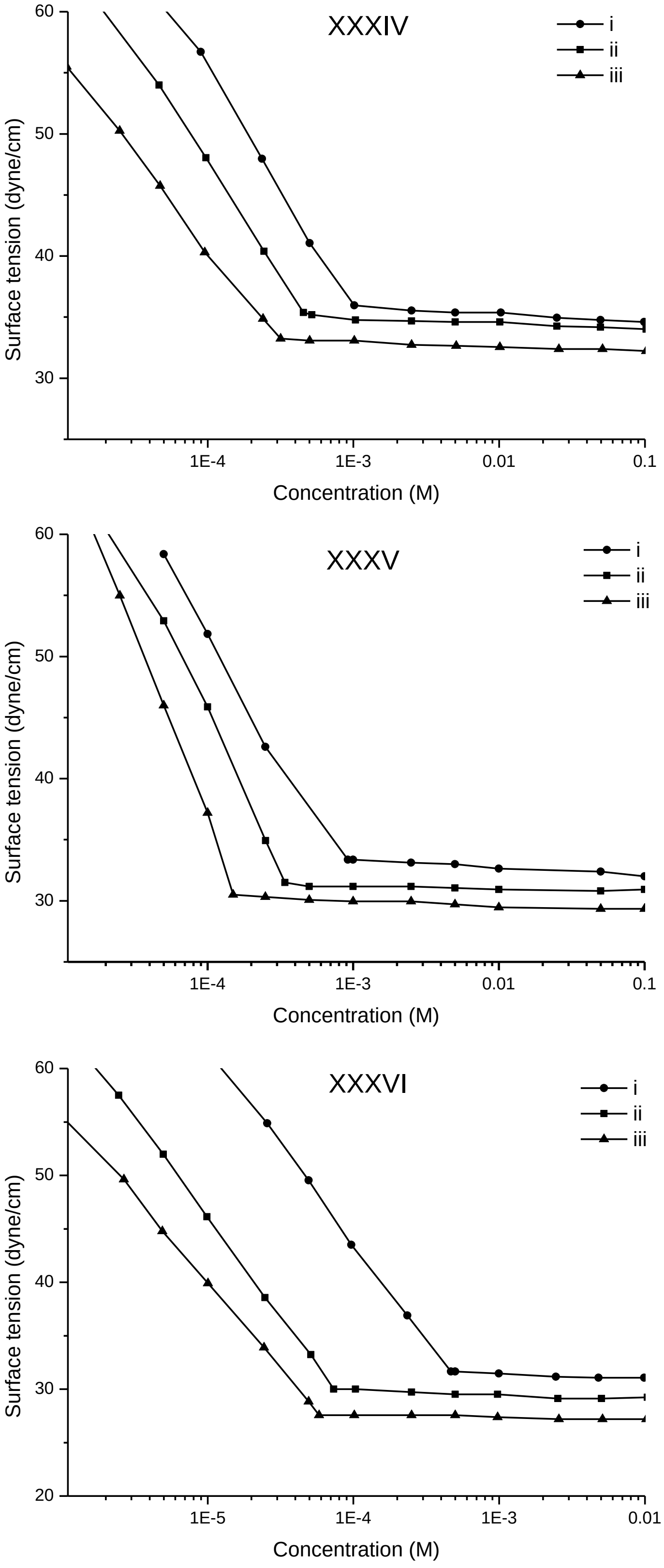


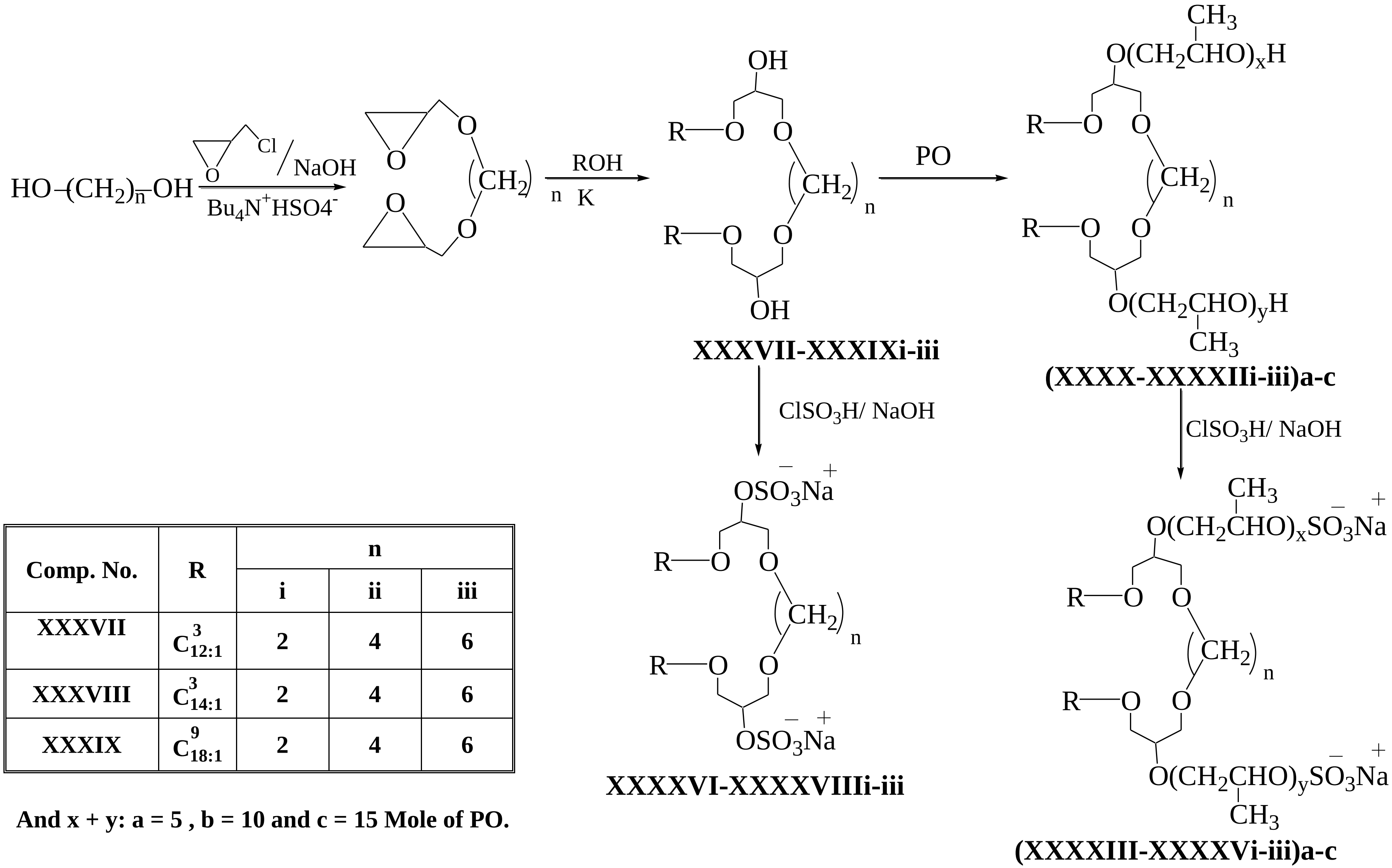
**Fig. 69:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXIV-XXXVI)i-iii.**

# Part (IV)

## Synthesis and surface properties of double tailed gemini surfactants derived from long chain fatty alcohol with diglycedyl ether:

Conventional surfactant molecules (single chained amphiphile) are composed of a long hydrophobic hydrocarbon tail with an ionic or polar hydrophilic head. A gemini (dimeric) surfactant consists of two conventional surfactant molecules chemically bonded together by a spacer. The two terminal hydrocarbon tails can be short or long, the two polar head groups can be cationic, anionic and nonionic. The spacer can be short (2, 4 and 6 methylene groups) or long.

We have synthesised a series of double chain gemini surfactants (nonionic, anionic-nonioinc and anionic) using 3-dodecenol, 3-tetradecenol and 9-octadecenol as a fatty alcohols. These compounds with various connecting groups (spacers) between the two lipophilic groups, were prepared by the reaction of glycol diglycidyl ethers (which prepared from the reaction of glycols (1,2-ethylene glycol, 1,4-butylene glycol and 1,6-hexylene glycol), with long chain fatty alcohols (3-dodecenol, 3-tetradecenol and 9- octadecenol) obtained from the reduction of corresponding alkenoic acid. Scheme 4 shows the synthetic methods to prepare these compounds. Their surface active properties were measured and the results were discussed.



| Comp. No. | R | n | | |
|---|---|---|---|---|
| | | i | ii | iii |
| **XXXVII** | $C^{3}_{12:1}$ | **2** | **4** | **6** |
| **XXXVIII** | $C^{3}_{14:1}$ | **2** | **4** | **6** |
| **XXXIX** | $C^{9}_{18:1}$ | **2** | **4** | **6** |

**And x + y: a = 5 , b = 10 and c = 15 Mole of PO.**

**Scheme 4**

## IV.a- Preparation of fatty alcohol:

The fatty alcohols of fatty acids (3-dodecenoic, 3- tetradecenoic or oleic acids) were prepared by reduction of the corresponding methyl ester using lithium aluminium hydride.

The structure of the fatty alcohols were confirmed *via* their IR, which revealed the presence of bands at 3420 cm$^{-1}$ corresponding to ν –OH and disappearance of ν –C=O band at 1711 cm$^{-1}$ corresponding to methyl ester (cf. Fig. 28, 29)

## IV.b- Preparation of glycol diglycidyl ether:

As discussed before in the preparation of diglycidyl ethers in part II, the glycol diglycidyl ethers were prepared from the reaction of epichchlorohydrin in the presence of sodium hydroxide and tetrabutyl-ammonium hydrogen sulphate with (ethylene glycol, 1,4-butylene glycol or 1,6-hexylene glycol). Fig. 30 show band at 1100 cm$^{-1}$ corresponding to ν –C–O–C– of ether linkage and at 851.8 cm$^{-1}$ corresponding to ν –C–O–C– of the epoxy ring, also it show the disappearance of the ν –OH band.

## IV.c- 1,10-Bis(dodec-3-enoxy)2,9-dihydroxy-4,7-dioxa-decan (XXXVIIi):

The reaction of diepoxide (ethylene glycol diglycidyl ether) with 3-dodecenol in the presence of potassium metal give 1,10-Bis(dodec-3-enoxy)2,9-dihydroxy-4,7-dioxa-decan (XXXVIIi). (Figs. 31, 49) show the IR and $^{1}$HNMR spectra of this compound, The IR spectrum revealed that, band at 1104 cm$^{-1}$ corresponding to ν –C–O–C– of ether linkage and band at 3482 cm$^{-1}$ corresponding to ν –OH. Where the $^{1}$HNMR spectrum shows the following data: δ = 0.87 (t, 6H, terminal $\underline{CH_3}$), 1.27 ( m, 32H, of alkyl chain), 2.00 (s, 2H, -<u>OH</u>), 3.24-3.59 (m, 16H, -O-<u>CH</u>$_2$), 3.91-3.93 (m, 2H, -CH$_2$-<u>CH</u>(OH)-CH$_2$), 5.342 (s, 4H, -<u>CH</u>=<u>CH</u>- ) see (fig. 49).

Three types of Gemini surfactants were prepared from this compound :

## IV.d- Nonionic gemini surfactants:

The nonionic gemini surfactants (XXXX-XXXXIIi-iii)a-c were obtained by the reaction of different moles of propylene oxide (5,10 and 15) with 1,ω-Bis(alkenoxy)-dihydroxy-dioxaalkan. The structures of the synthesized nonionic gemini surfactants were confirmed via IR and $^1$HNMR spectrum. IR of the compounds (XXXXi)a-c exhibit characteristic bands of the ether linkage of polypropenoxy chain (ν -C-O-C) at 1107-1115 cm$^{-1}$. (*cf.* fig. 32-34). The $^1$HNMR spectrum of XXXXi-a showed that, the characteristic protons of propenoxy group at δ = 3.36- 4.04 ppm (*cf.* Fig 50). The surface active properties of these surfactants were listed in (tables 42-44).

## IV.e- Anionic- nonionic surfactants:

The sulfation of nonionic surfactants have a considerable effect on the properties, because the changes of oxylakylated compound from nonionic to anionic surface active agents, and the product is like an ether alcohol sulphate, and have both anionic and nonionic characteristics. The nonionic Gemini surfactants were sulfated with chlorosulfonic acid followed by neutralization via sodium hydroxide. Tables 45-47 showed the surface active properties of the compounds ((XXXXIII-XXXXVi-iii)a-c

## IV.f- Anionic surfactants:

The anionic gemini surfactants with spacers have been prepared from 1,ω-Bis(alkenoxy)-dihydroxydioxaalkan according to the conventional procedure used for classical surfactants to give (XXXXVI-XXXXVII)Ii-iii.

The $^1$HNMR spectrum of (XXXXVIi)(fig. 51) showed the disappearance of –OH protons when compared with (fig. 49). Also it confirmed by elemental analysis which listed in (table 59). The surface active properties of these surfactants were listed in (table 48).

## ***Surface active properties and related properties:***

The surface activity and related properties of the Gemini surfactants derived from 1,ω-bis(alkenoxy)dihydroxydioxaalkan are listed in (tables 42-48).

### 1- Surface and Interfacial tensions :

All double chain gemini surfactants (nonionic, anionic-nonionic and anionic) show satisfied values of surface and interfacial tension. Where the anionic gemini surfactants (XXXXVI-XXXXVIII)i-iii have the lowest value of surface tension. Moreover, the surface tension decrease with increasing the number of carbon atoms of the spacer in anionic surfactants, while in other two types of corresponding gmini surfactants this effect of spacers is not clear.

### 2- Kraft point :

The Kraft point for all anionic compounds was below 0°C s. These compounds have a great solubility in water, This great increase in water solubility of these compounds is believed to be due to the combined effect of two ionic groups and the ether oxygen atoms in the connecting group(141).

### 3-Cloud point:

The cloud points of the nonionic gemini surfactants (XXXX-XXXXIIi-iii)a-c were listed in (tables 42-44), it is seen that, these surfactants have moderately cloud points and its increase as the propylene oxide units increase in the surfactants molecule which is the hydrophilic part(123). The cloud point of 1,ω-bis(octadexc-9-enoxy)dihydroxydioxaalkan (XXXXIIi-iii)a with 5 mole of propylene oxide, all are insoluble at room temperature and gave turbid solutions.

On the other hand, the spacers show a little effect on the cloud point while as the chain length of the spacer increased the cloud point decreased, and that may be due to the increasing of the hydrophobicity of the molecule.

## 3- Wetting time :

From the data listed in (tables 42-48) we can conclude that, the wetting time increased as increasing the length of the hydrophobic group.

Maximum wetting efficiency of any given surfactant often is observed at the lowest number of propylene oxide units in the surfactants molecules ( 5 mole PO).

Actually the increase in the spacer length increase the percent of hydrophobic part in the surfactant molecule so it was noticed that with increasing the spacer length the wetting time increased.

## 4- Emulsifying properties :

The emulsion stability increased as the chain length increased. And it also recorded that, the nonionic gemini surfactants have much higher emulsion stability than other types of gemini surfactants (*cf*. tables (42-48)).

We can also notice, the spacer effect on the emulsion stability, while increases with increasing the spacer length. The introducing of ionic groups into nonionic compounds decrease the emulsification stability, while those which are completely ionic have a lowest emulsification power.

## 5- Foaming power :

The foaming properties of gemini surfactants depend, as in conventional surfactants, upon the chain length of the hydrophobic groups. Where increases with increasing the chain length.

As shown in Table 48, the anionic gemini surfactants have the highest foam.

When we study the spacer effect on the foam height we can’t see a large variety from foam height, so we can conclude that, the structure of the spacer does not influence the foam height to a large extent, where other study show the same results but it also obtained that the spacer length seems to be an important parameter for the stability(204).

## 6- Critical micelle concentration (CMC) :

The CMC and γcmc values are listed in (tables 42-48). These data are also represented in (figs. 70-76). It is seen that, Geminis with an anionic hydrophile show higher CMC values than nonionic gemini surfactants.

Furthermore, in case of ionic gemini surfactants, the value of *CMC* decrease with increasing the spacer length under the range of study, this decreasing can be attributed to that, the short spacer increased the intermolecular repulsion between head groups, on the other hand in case of long spacer, the spacer shields the head group’s repulsion. This leads to micelle formation at low concentration(159).

One of the main reasons for the current interest in dimeric surfactants is that their *CMC* are much lower than those of the corresponding conventional surfactants this mainly because two alkyl chains, rather than one, are transferred at a time from water to the micelle (205).

## 7- Biodegradability :

Tables 49-55 shows the following facts, the biodegradability decreases as the number of propylene oxide units increased in the surfactant molecules, as the chain length increase the biodegradability decrease, the anionic surfactants have much higher biodegradability than nonionic surfactants.

Table(41): **Elemental analysis of 1,ω-bis(alkenoxy)-dihydroxy-dioxaalkane:**

| Comp. No. | M. Formula | M. Wt. | C% | | H% | | S% | |
|---|---|---|---|---|---|---|---|---|
| | | | Calc. | Found | Calc. | Found | Calc. | Found |
| XXXXVIi | $C_{32}H_{60}O_{12}S_2Na_2$ | 746.92 | 51.46 | 50.94 | 8.10 | 7.70 | 8.59 | 7.81 |
| XXXXVIii | $C_{34}H_{64}O_{12}S_2Na_2$ | 774.98 | 52.69 | 51.80 | 8.32 | 7.84 | 8.28 | 7.50 |
| XXXXVIiii | $C_{36}H_{68}O_{12}S_2Na_2$ | 803.03 | 53.84 | 53.00 | 8.54 | 7.20 | 7.99 | 7.33 |
| XXXXVIIi | $C_{36}H_{68}O_{12}S_2Na_2$ | 80.3.03 | 53.84 | 52.98 | 8.54 | 8.10 | 7.99 | 7.00 |
| XXXXVIIii | $C_{38}H_{72}O_{12}S_2Na_2$ | 831.08 | 54.92 | 53.42 | 8.73 | 7.95 | 7.72 | 7.32 |
| XXXXVIIiii | $C_{40}H_{76}O_{12}S_2Na_2$ | 859.14 | 55.92 | 54.56 | 8.92 | 7.98 | 7.46 | 6.80 |
| XXXXVIIIi | $C_{44}H_{84}O_{12}S_2Na_2$ | 915.24 | 57.74 | 56.02 | 9.25 | 8.24 | 7.01 | 6.80 |
| XXXXVIIIii | $C_{46}H_{88}O_{12}S_2Na_2$ | 943.30 | 58.57 | 57.19 | 9.40 | 8.80 | 6.80 | 6.57 |
| XXXXVIIIiii | $C_{48}H_{92}O_{12}S_2Na_2$ | 971.35 | 59.35 | 57.99 | 9.55 | 8.67 | 6.60 | 6.01 |

Table(42): **Surface properties of oxypropenoxylated 1, ω-bis(dodec-3-enoxy)-dihydroxy-dioxa-alkane:**

| Compound No. | Ȓ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXi-a | $C_2$ | 5 | 40 | 8 | 49 | 49 | 60 | 30 | 0.90 | 41 |
| XXXXi-b | $C_2$ | 10 | 41 | 9 | 54 | 58 | 55 | 40 | 0.75 | 42.5 |
| XXXXi-c | $C_2$ | 15 | 42.5 | 11.5 | 59 | 65 | 52 | 50 | 0.63 | 44 |
| XXXXii-a | $C_4$ | 5 | 39 | 9 | 52 | 53 | 64 | 30 | 0.85 | 40 |
| XXXXii-b | $C_4$ | 10 | 41 | 10 | 55 | 60 | 59 | 50 | 0.72 | 42 |
| XXXXii-c | $C_4$ | 15 | 43 | 12 | 58 | 74 | 54 | 80 | 0.65 | 44 |
| XXXXiii-a | $C_6$ | 5 | 41 | 8.5 | 50 | 42 | 63 | 40 | 0.86 | 43 |
| XXXXiii-b | $C_6$ | 10 | 43.5 | 10 | 49 | 39 | 62 | 60 | 0.76 | 45 |
| XXXXiii-c | $C_6$ | 15 | 44 | 11 | 56 | 66 | 56 | 80 | 0.60 | 46 |

**n = number of PO. units**

Table(43): **Surface properties of oxypropenoxylated 1,ω-bis(tetradec-3-enoxy)-dihydroxy-dioxa-alkane:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point $^{o}$C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXIi-a | $C_2$ | 5 | 37 | 10 | 44 | 58 | 66 | 30 | 0.75 | 39 |
| XXXXIi-b | $C_2$ | 10 | 37 | 11 | 58 | 67 | 59 | 40 | 0.60 | 39.5 |
| XXXXIi-c | $C_2$ | 15 | 39 | 11.5 | 60 | 77 | 56 | 60 | 0.55 | 41.5 |
| XXXXIii-a | $C_4$ | 5 | 39 | 9 | 48 | 56 | 63 | 30 | 0.71 | 40 |
| XXXXIii-b | $C_4$ | 10 | 40 | 10 | 54 | 60 | 64 | 50 | 0.55 | 42 |
| XXXXIii-c | $C_4$ | 15 | 41.5 | 11 | 58 | 80 | 58 | 65 | 0.50 | 43.5 |
| XXXXIiii-a | $C_6$ | 5 | 39 | 10 | 47 | 60 | 74 | - | 0.72 | 42 |
| XXXXIiii-b | $C_6$ | 10 | 41 | 11 | 52 | 69 | 64 | 40 | 0.53 | 43.5 |
| XXXXIiii-c | $C_6$ | 15 | 43.5 | 12.5 | 56 | 77 | 61 | 70 | 0.45 | 45 |

**n = number of PO. units**

Table (44): **Surface properties of oxypropenoxylated 1,ω -bis(octadec-9-enoxy)-dihydroxy-dioxa-alkane:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Cloud Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXIIi-a | $C_2$ | 5 | 40 | 11 | 30 | 64 | 99 | - | 0.31 | 41 |
| XXXXIIi-b | $C_2$ | 10 | 42 | 12 | 45 | 68 | 81 | 30 | 0.29 | 45 |
| XXXXIIi-c | $C_2$ | 15 | 43.5 | 13 | 49 | 76 | 75 | 50 | 0.20 | 45.5 |
| XXXXIIii-a | $C_4$ | 5 | 40 | 10 | 30 | 70 | 91 | - | 0.35 | 40 |
| XXXXIIii-b | $C_4$ | 10 | 42 | 12 | 40 | 72 | 84 | 40 | 0.25 | 43 |
| XXXXIIii-c | $C_4$ | 15 | 44 | 12.5 | 60 | 78 | 79 | 60 | 0.20 | 45.5 |
| XXXXIIiii-a | $C_6$ | 5 | 42.5 | 10.5 | 30 | 78 | 98 | - | 0.30 | 43 |
| XXXXIIiii-b | $C_6$ | 10 | 43 | 11 | 45 | 81 | 89 | 45 | 0.21 | 46 |
| XXXXIIiii-c | $C_6$ | 15 | 44.5 | 13 | 60 | 83 | 80 | 60 | 0.15 | 48 |

**n = number of PO. units**

Table (45): **Surface properties of oxypropenoxylated 1, ω -bis(dodec-3-enoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXIIIi-a | $C_2$ | 5 | 37 | 11 | < 0 | 60 | 4 : 05 | 130 | 3.0 | 39 |
| XXXXIIIi-b | $C_2$ | 10 | 38 | 12 | < 0 | 60 | 3 : 50 | 120 | 2.0 | 41 |
| XXXXIIIi-c | $C_2$ | 15 | 40 | 12.5 | < 0 | 75 | 3 : 50 | 90 | 1.5 | 42.5 |
| XXXXIIIii-a | $C_4$ | 5 | 36 | 9 | < 0 | 63 | 4 : 10 | 150 | 2.5 | 36 |
| XXXXIIIii-b | $C_4$ | 10 | 36 | 11 | < 0 | 69 | 3 : 48 | 130 | 2.0 | 38 |
| XXXXIIIii-c | $C_4$ | 15 | 38 | 12 | < 0 | 78 | 4 : 00 | 100 | 1.0 | 40 |
| XXXXIIIiii-a | $C_6$ | 5 | 36 | 9 | < 0 | 67 | 4 : 50 | 150 | 2.0 | 36 |
| XXXXIIIiii-b | $C_6$ | 10 | 34.5 | 11 | < 0 | 71 | 4 : 40 | 130 | 1.5 | 38 |
| XXXXIIIiii-c | $C_6$ | 15 | 37 | 11.5 | < 0 | 74 | 4 : 00 | 120 | 0.90 | 39 |

**n = number of PO. units**

Table (46): **Surface properties of oxypropenoxylated 1,ω-bis(tetradec-3-enoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | Ȓ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point °C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXIVi-a | $C_2$ | 5 | 35 | 9 | < 0 | 55 | 4 : 10 | 150 | 2.7 | 37 |
| XXXXIVi-b | $C_2$ | 10 | 36 | 9 | < 0 | 75 | 3 : 50 | 140 | 1.8 | 39 |
| XXXXIVi-c | $C_2$ | 15 | 37.5 | 10.5 | < 0 | 80 | 3 : 20 | 110 | 1.0 | 40 |
| XXXXIVii-a | $C_4$ | 5 | 35 | 10 | < 0 | 70 | 4 : 00 | 150 | 0.90 | 37 |
| XXXXIVii-b | $C_4$ | 10 | 35.5 | 11 | < 0 | 75 | 3 : 50 | 140 | 0.70 | 38 |
| XXXXIVii-c | $C_4$ | 15 | 37 | 12 | < 0 | 79 | 3 : 30 | 120 | 0.45 | 41 |
| XXXXIViii-a | $C_6$ | 5 | 33 | 10 | < 0 | 74 | 5 : 10 | 150 | 0.80 | 35 |
| XXXXIViii-b | $C_6$ | 10 | 34 | 11 | < 0 | 78 | 4 : 40 | 130 | 0.65 | 37 |
| XXXXIViii-c | $C_6$ | 15 | 36 | 12.5 | < 0 | 81 | 4 : 15 | 110 | 0.50 | 39 |

**n = number of PO. units**

Table (47): **Surface properties of oxypropenoxylated 1,ω -bis(octadec-9-enoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R̀ | n | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point $^{o}$C 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXVi-a | $C_2$ | 5 | 32 | 11 | < 0 | 50 | 4 : 45 | 170 | 0.50 | 34 |
| XXXXVi-b | $C_2$ | 10 | 33 | 10 | < 0 | 45 | 4 : 30 | 160 | 0.30 | 35 |
| XXXXVi-c | $C_2$ | 15 | 34.5 | 12 | < 0 | 65 | 4 : 15 | 150 | 0.25 | 38 |
| XXXXVii-a | $C_4$ | 5 | 33 | 9 | < 0 | 60 | 5 : 00 | 160 | 0.25 | 36 |
| XXXXVii-b | $C_4$ | 10 | 34 | 10 | < 0 | 63 | 4 : 50 | 160 | 0.10 | 38 |
| XXXXVii-c | $C_4$ | 15 | 36 | 11 | < 0 | 75 | 4 : 10 | 150 | 0.09 | 40 |
| XXXXViii-a | $C_6$ | 5 | 31 | 12 | < 0 | 66 | 5 : 20 | 170 | 0.10 | 35 |
| XXXXViii-b | $C_6$ | 10 | 33 | 11 | < 0 | 74 | 5 : 00 | 150 | 0.08 | 36 |
| XXXXViii-c | $C_6$ | 15 | 33.5 | 11.5 | < 0 | 82 | 4 : 49 | 130 | 0.06 | 39 |

**n = number of PO. units**

Table (48): **Surface properties of 1,ω-bis(alkenoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R | R̀ | Surface tension (dyne/cm) 0.1 % | Interfacial tension (dyne/cm) 0.1 % | Kraft Point $^{o}C$ 1.0 % | Wetting time (Second) 1.0 % | Emulsion stability (min : Sec.) 1.0 % | Foam height (mm) 1.0 % | CMC (M) $10^{-4}$ | $\gamma_{CMC}$ (Dyne/cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| XXXXVIi | $C_{12}$ | $C_2$ | 35 | 12 | < 0 | 54 | 2 : 30 | 210 | 5.0 | 36 |
| XXXXVIii | $C_{12}$ | $C_2$ | 34 | 11 | < 0 | 65 | 3 : 00 | 230 | 4.0 | 34.5 |
| XXXXVIiii | $C_{12}$ | $C_2$ | 32 | 11 | < 0 | 75 | 2 : 50 | 230 | 2.5 | 33.5 |
| XXXXVIIi | $C_{14}$ | $C_4$ | 36 | 10 | < 0 | 53 | 2 : 30 | 230 | 3.1 | 35 |
| XXXXVIIii | $C_{14}$ | $C_4$ | 32 | 9 | < 0 | 75 | 2 : 55 | 240 | 1.5 | 34 |
| XXXXVIIiii | $C_{14}$ | $C_4$ | 31 | 8.5 | < 0 | 85 | 3 : 10 | 240 | 0.90 | 32 |
| XXXXVIIIi | $C_{18}$ | $C_6$ | 30 | 12 | < 0 | 73 | 3 : 05 | 250 | 0.62 | 30 |
| XXXXVIIIii | $C_{18}$ | $C_6$ | 28 | 10 | < 0 | 90 | 3 : 40 | 260 | 0.44 | 31 |
| XXXXVIIIiii | $C_{18}$ | $C_6$ | 27 | 11 | < 0 | 120 | 4 : 10 | 270 | 0.32 | 29 |

Table (49): **Biodegradability of oxypropenoxylated 1, ω -bis(dodec-3-enoxy)-dihydroxy-dioxa-alkane:**

| Compound No. | Ȑ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXi-a | $C_2$ | 5 | 46 | 56 | 60 | 66 | 74 | 85 | 96 |
| XXXXi-b | $C_2$ | 10 | 42 | 53 | 58 | 64 | 71 | 81 | 95 |
| XXXXi-c | $C_2$ | 15 | 36 | 51 | 55 | 61 | 69 | 83 | 93 |
| XXXXii-a | $C_4$ | 5 | 44 | 53 | 59 | 64 | 72 | 80 | 91 |
| XXXXii-b | $C_4$ | 10 | 41 | 52 | 57 | 62 | 69 | 78 | 89 |
| XXXXii-c | $C_4$ | 15 | 39 | 49 | 54 | 61 | 66 | 76 | 87 |
| XXXXiii-a | $C_6$ | 5 | 40 | 49 | 57 | 61 | 69 | 78 | 89 |
| XXXXiii-b | $C_6$ | 10 | 37 | 48 | 55 | 59 | 66 | 75 | 85 |
| XXXXiii-c | $C_6$ | 15 | 35 | 45 | 51 | 57 | 61 | 72 | 83 |

**n = number of PO. units**

Table (50): **Biodegradability of oxypropenoxylated 1,ω-bis(tetradec-3-enoxy)-dihydroxy-dioxa-alkane:**

| Compound No. | Ȑ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXIi-a | $C_2$ | 5 | 42 | 53 | 60 | 70 | 75 | 80 | 93 |
| XXXXIi-b | $C_2$ | 10 | 39 | 50 | 58 | 64 | 72 | 77 | 91 |
| XXXXIi-c | $C_2$ | 15 | 37 | 48 | 55 | 63 | 68 | 76 | 89 |
| XXXXIii-a | $C_4$ | 5 | 40 | 52 | 57 | 62 | 70 | 79 | 87 |
| XXXXIii-b | $C_4$ | 10 | 37 | 49 | 54 | 60 | 69 | 76 | 85 |
| XXXXIii-c | $C_4$ | 15 | 35 | 46 | 52 | 58 | 65 | 74 | 81 |
| XXXXIiii-a | $C_6$ | 5 | 37 | 47 | 52 | 60 | 65 | 75 | 84 |
| XXXXIiii-b | $C_6$ | 10 | 36 | 45 | 50 | 57 | 63 | 73 | 81 |
| XXXXIiii-c | $C_6$ | 15 | 34 | 43 | 48 | 53 | 62 | 70 | 79 |

**n = number of PO. units**

Table (51) : **Biodegradability of oxypropenoxylated 1,ω-bis(octadec-9-enoxy)-dihydroxy-dioxa-alkane:**

| Compound No. | R̀ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXIIi-a | $C_2$ | 5 | 40 | 45 | 58 | 62 | 70 | 73 | 85 |
| XXXXIIi-b | $C_2$ | 10 | 38 | 43 | 55.5 | 60 | 68 | 70 | 82 |
| XXXXIIi-c | $C_2$ | 15 | 34 | 40 | 53 | 57 | 65 | 68 | 79 |
| XXXXIIii-a | $C_4$ | 5 | 36 | 45 | 52 | 56.5 | 66 | 73.5 | 83 |
| XXXXIIii-b | $C_4$ | 10 | 33 | 43 | 49.5 | 58 | 65 | 72 | 81 |
| XXXXIIii-c | $C_4$ | 15 | 31 | 41 | 47 | 55 | 62.5 | 70 | 79 |
| XXXXIIiii-a | $C_6$ | 5 | 34 | 40 | 46 | 54 | 68 | 71 | 81 |
| XXXXIIiii-b | $C_6$ | 10 | 31 | 38.5 | 43 | 51 | 65 | 69.5 | 79 |
| XXXXIIiii-c | $C_6$ | 15 | 29 | 37 | 40 | 69 | 63 | 68 | 76 |

**n = number of PO. units**

Table (52): **Biodegradability of oxypropenoxylated 1, ω-bis(dodec-3-enoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R̀ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXIIIi-a | $C_2$ | 5 | 46 | 58 | 61 | 73 | 88 | 92 | - |
| XXXXIIIi-b | $C_2$ | 10 | 43 | 55 | 59 | 71 | 86 | 90 | 98 |
| XXXXIIIi-c | $C_2$ | 15 | 40 | 52.5 | 58 | 69 | 84.5 | 89 | 95 |
| XXXXIIIii-a | $C_4$ | 5 | 47 | 53 | 60 | 71 | 77 | 84 | - |
| XXXXIIIii-b | $C_4$ | 10 | 45 | 51 | 58 | 69 | 75 | 81 | 97 |
| XXXXIIIii-c | $C_4$ | 15 | 43 | 49 | 56.5 | 67 | 73.5 | 79 | 95 |
| XXXXIIIiii-a | $C_6$ | 5 | 45 | 53 | 64 | 74 | 75 | 81 | - |
| XXXXIIIiii-b | $C_6$ | 10 | 43 | 50 | 62 | 72 | 73 | 78 | 96 |
| XXXXIIIiii-c | $C_6$ | 15 | 40 | 47 | 59.5 | 69 | 71.5 | 76 | 94 |

**n = number of PO. units**

## Table (53): **Biodegradability of oxypropenoxylated 1,ω-bis(tetradec-3-enoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | Ȓ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXIVi-a | $C_2$ | 5 | 45 | 58 | 65 | 70 | 81 | 89 | - |
| XXXXIVi-b | $C_2$ | 10 | 42 | 55 | 63 | 68 | 79 | 87 | 97 |
| XXXXIVi-c | $C_2$ | 15 | 39 | 53 | 59 | 66 | 76 | 85 | 95 |
| XXXXIVii-a | $C_4$ | 5 | 44 | 55 | 62 | 70 | 80 | 87 | - |
| XXXXIVii-b | $C_4$ | 10 | 41 | 52 | 59 | 68 | 78 | 86 | 96 |
| XXXXIVii-c | $C_4$ | 15 | 38 | 49.5 | 56 | 65.5 | 77 | 84 | 93 |
| XXXXIViii-a | $C_6$ | 5 | 43 | 52 | 59 | 67 | 78.5 | 85 | 92 |
| XXXXIViii-b | $C_6$ | 10 | 41 | 49 | 57 | 65 | 75 | 83 | 90 |
| XXXXIViii-c | $C_6$ | 15 | 39 | 45 | 54 | 63 | 74 | 80 | 88 |

**n = number of PO. units**

Table (54): **Biodegradability of oxypropenoxylated oxypropenoxylated 1,ω-bis(octadec-9-enoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R̀ | n | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXVi-a | $C_2$ | 5 | 43 | 50 | 62 | 69 | 77 | 88 | 96 |
| XXXXVi-b | $C_2$ | 10 | 40 | 49 | 59 | 66 | 74 | 85 | 93 |
| XXXXVi-c | $C_2$ | 15 | 39 | 46 | 56 | 64 | 72.5 | 84 | 91 |
| XXXXVii-a | $C_4$ | 5 | 38.5 | 48 | 59 | 66 | 71 | 81 | 89 |
| XXXXVii-b | $C_4$ | 10 | 37 | 47 | 54 | 63.5 | 69 | 79 | 87 |
| XXXXVii-c | $C_4$ | 15 | 35 | 45 | 52 | 62 | 68 | 77 | 84 |
| XXXXViii-a | $C_6$ | 5 | 37 | 46 | 57 | 61 | 70 | 80 | 87 |
| XXXXViii-b | $C_6$ | 10 | 33.5 | 43 | 54 | 60 | 68 | 78 | 85 |
| XXXXViii-c | $C_6$ | 15 | 35 | 40.5 | 53 | 57 | 66 | 75 | 83 |

**n = number of PO. units**

Table (55) : **Biodegradability of 1,ω-bis(alkenoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R | R̀ | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 7th day |
|---|---|---|---|---|---|---|---|---|---|
| XXXXVIi | $C_{12}$ | $C_2$ | 67 | 77 | 84 | 89 | 94 | - | - |
| XXXXVIii | $C_{12}$ | $C_4$ | 63 | 70 | 79 | 86 | 92 | 97 | - |
| XXXXVIiii | $C_{12}$ | $C_6$ | 60 | 69 | 78 | 85 | 89 | 95 | - |
| XXXXVIIi | $C_{14}$ | $C_2$ | 61 | 75 | 80 | 88 | 93 | 97 | - |
| XXXXVIIii | $C_{14}$ | $C_4$ | 58 | 72 | 78 | 82 | 88 | 93 | - |
| XXXXVIIiii | $C_{14}$ | $C_6$ | 56.5 | 69 | 73 | 80 | 87.5 | 94 | - |
| XXXXVIIIi | $C_{18}$ | $C_2$ | 57 | 68 | 74 | 81 | 87 | 94 | 98 |
| XXXXVIIIii | $C_{18}$ | $C_4$ | 55 | 66.5 | 72 | 79 | 84 | 90 | 95 |
| XXXXVIIIiii | $C_{18}$ | $C_6$ | 54 | 63 | 69 | 76 | 83 | 89 | 95 |

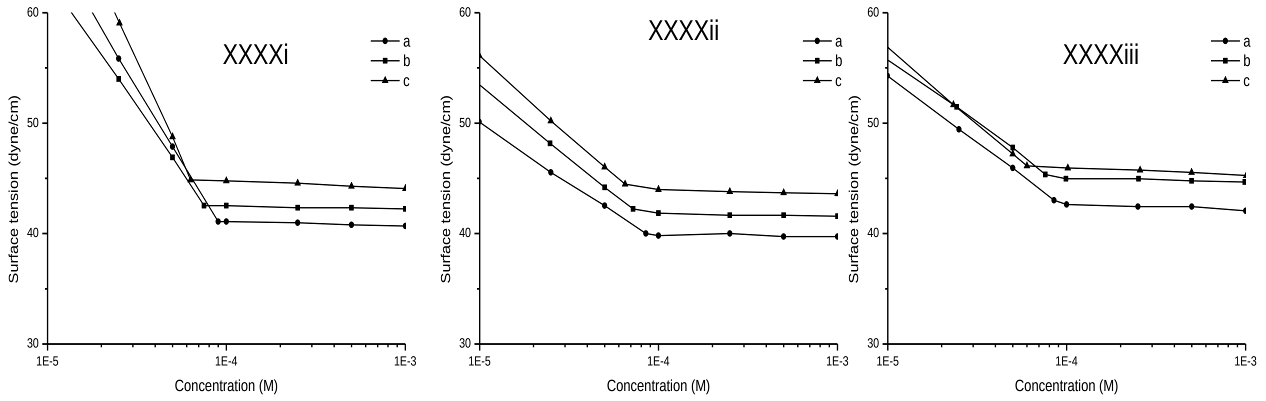


**Fig.70:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXi-iii)a-c.**

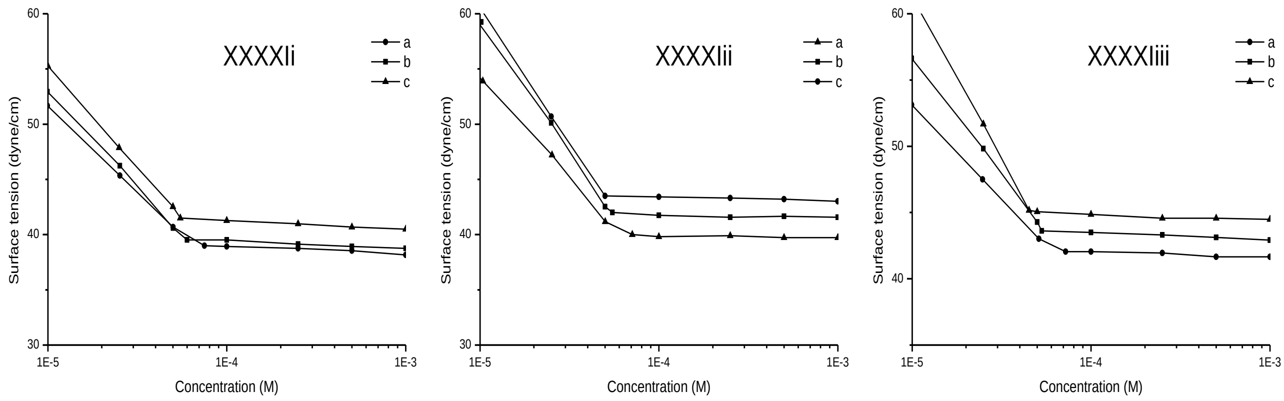


**Fig. 71:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXIi-iii)a-c.**

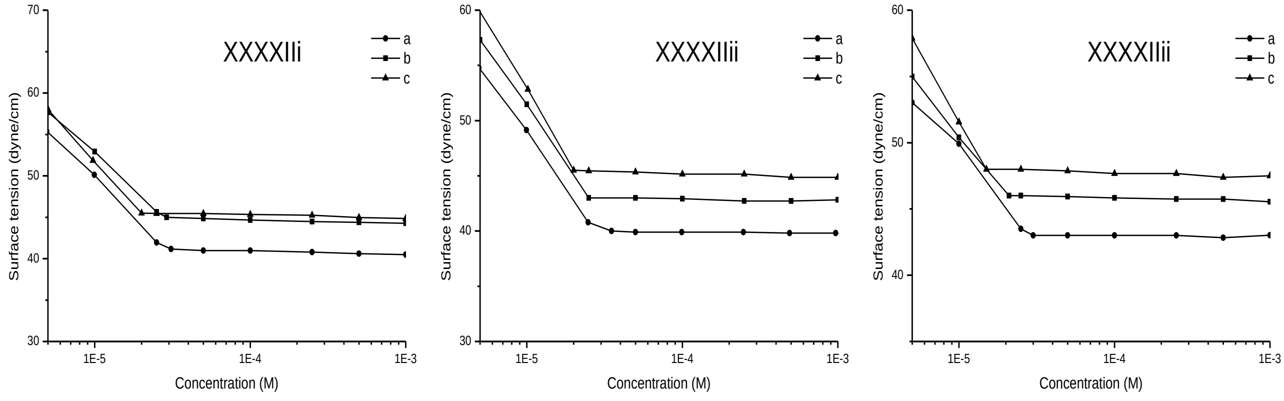


**Fig. 72:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXIIi-iii)a-c.**

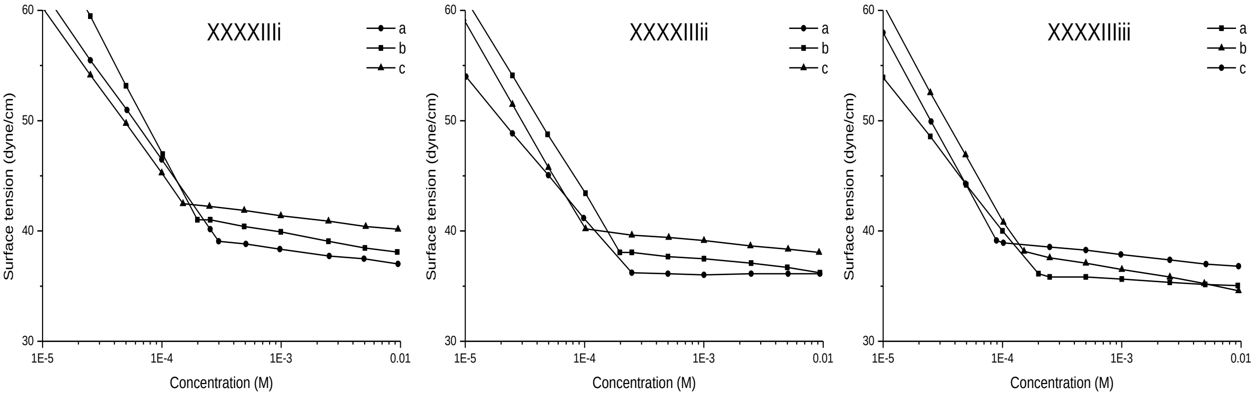


Fig.73:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXIIIi-iii)a-c.

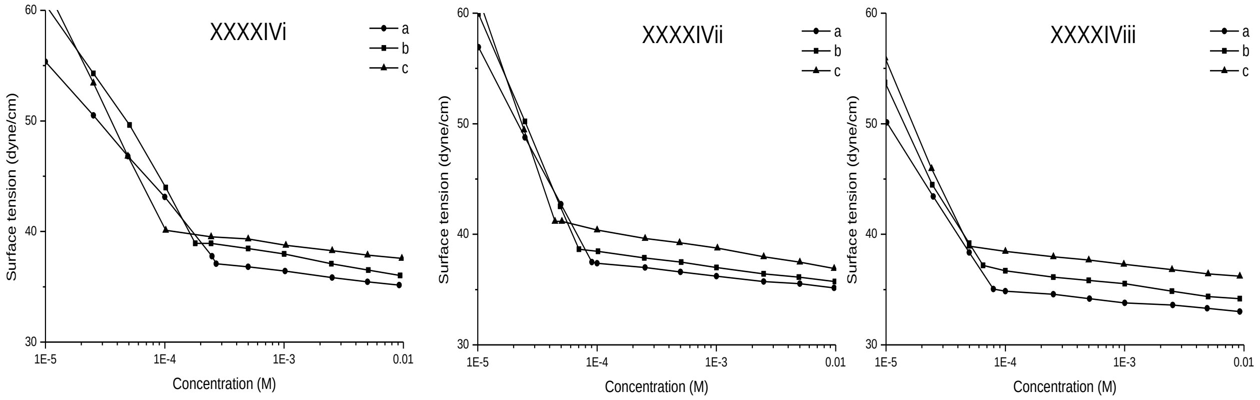


Fig. 74:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXIVi-iii)a-c.

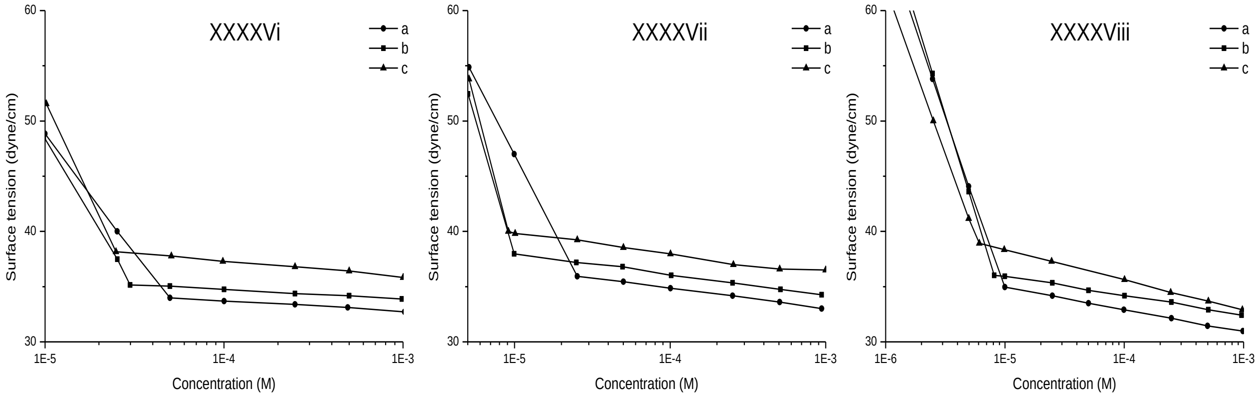


Fig.75:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXVi-iii)a-c.

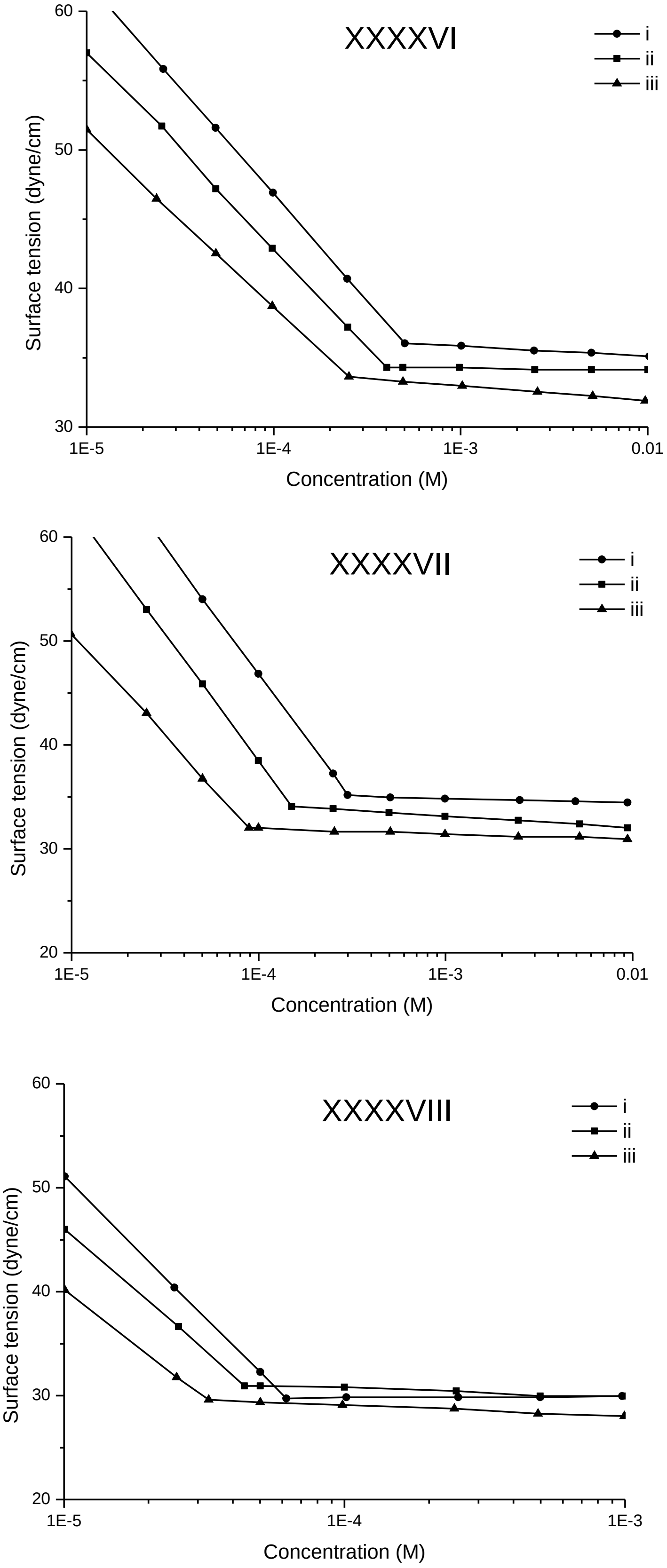


**Fig.76:The plot of surface tension versus the logarithmic molar surfactant concentration of the (XXXXVI-XXXXVIII)**

# Part (V)

## Thermodynamic Parameters

Surface activity and micellar properties of surfactants are of potential importance and scientific interest. Surfactants micellize in solution after a critical concentration depends on their molecular structure and environmental conditions (206). The concept of the CMC value is very useful and perhaps the most frequently measured and discussed micellar parameter. Surface tension is one of the widely used physico-chemical property at a gas–liquid interface to determine CMC value without serious difficulty. Through surface tension versus surfactant concentration curves, several surface and thermodynamic parameters are derived (207). Detailed thermodynamics of micellization and adsorption processes are essential for understanding their behaviour in their media, stability, spontaneity of formation and the state of environmental order or disorder. So the determination of thermodynamic parameters of micellization and adsorption has played an important role in developing and understanding the behaviour of the surfactants in their media.

Three series of the three types of gemini surfactants (XXIIi-XXIVi), (XXXIVii- XXXVIii) and (XXXXVIi- XXXXVIIIi) synthesized in this study were chosen as representative sample to study the surface and thermodynamic parameters.

## Surface parameters:

### (i) Surface tension and critical micelle concentration:

Values of surface tension “$\gamma$” at different temperatures (30, 40 and 50$^{o}$C) were plotted versus the logarithmic molar surfactant concentration, and the critical micelle concentration “CMCs” values were determined from this curves at each temperature. Both surface tension at CMC “$\gamma$cmc” and

–logCMC were listed in (table 56-58). It was found that, increasing the temperature decreased the surface tension of these anionic surfactants, and their critical micelle concentration (CMC) was increased. This result was due to an increase in the repulsion forces between the polar hydrophilic groups, which encouraged micellization at higher concentrations.

### *(ii) Effectiveness ($\pi_{CMC}$):*

The difference between the surface tension of these anionic gemini surfactants at their CMC and that of pure water is termed “effectiveness” ($\pi_{CMC}$) (208):

$$\pi_{cmc} = \gamma_o - \gamma$$

where “$\gamma_o$” is the surface tension of the pure water and “$\gamma$” is the surface tension of the surfactant solution at CMC.

The more efficient is one that gives the greater lowering in surface tension for the critical micelle concentration. Increasing the number of methylene groups (–CH2–) along the hydrophobic chains increases the hydrophobicity of the molecules, hence water–hydrophobe interactions increase which decreases the surface tension, followed by increase the effectiveness.

The effectiveness of the these surfactants ranged between 35.5 and 46 dyn/cm. Increasing the temperature increased the effectiveness of the surfactant solutions.

### *(iii) Maximum surface excess ( $\Gamma_{max}$):*

The maximum surface excess of the synthesized gemini surfactants (Table 56-58) was calculated using a modified form of the Gibbs equation at CMC(209):

$$\Gamma_{max} = -1/RT(\partial\gamma/\partial \log C)$$

The chemical nature of the hydrophobic chains played an important role in the value of surface excess adsorption.□ The maximum surface excess values showed a high accumulation of surfactant molecules with longer hydrophobic chains. This is due to the increase in repulsion force between these molecules and water molecules, which drives the surfactants to the air surface. The increasing value of $\Gamma_{max}$ also indicates the tendency of these molecules toward adsorption at the interface. The data obtained for $\Gamma_{max}$ are presented in (Table 56-58) show that, in all series there is a slight increase in $\Gamma_{max}$ with the increase in the alkyl chain length.

Compound (XXIVi) with triple chain gemini surfactant show the higher value of maximum surface excess. It indicated that, as the temperature increase the maximum surface excess decrease.

## *(iv) Minimum surface area ($A_{min}$)(210):*

The minimum surface area ($A_{min}$) of surfactant molecules is defined as the average area occupied by each surfactant molecule on the air–water interface. The area occupied by each compound at the air/water interface could be calculated according to Gibbs equation in the following formula:

$$A_{min} = 1/\Gamma_{max} \,.\, N_A$$

Where $N_A$ is Avogadro’s number and $\Gamma_{max}$ is the maximum surface excess.

Increasing the surface concentration (surface pressure, $\partial\gamma/\partial \log C$) increased the number of surfactant molecules at the interface; hence, some sort of crowding occurred as $\Gamma_{max}$ increased and the area available for each molecule at the interface decreased (208). From the data in (Table 56-58), it can be concluded that increasing the hydrophobic chain length decreased the area available to the surfactant molecules at the interface. Also, the data show that, $A_{min}$ increases with increasing temperature as a result of increasing the molecular motion.

## (V) Thermodynamic Parameters of Micellization of Gemini Amphiphiles:

According to the Gibb's equations of thermodynamics, the thermodynamic functions of micellization including, free energy, entropy and enthalpy change (ΔG, ΔS, ΔH, respectively) were calculated from the surface parameter data listed in (Table 81) according to the following equations(211):

$$\Delta G_{mic} = -\ 2.303\ RT \log (CMC),$$

$$\Delta S_{mic} = \partial \Delta G_{mic} / \partial T \quad \text{and}$$

$$\Delta H_{mic} = \Delta G_{mic} + T\,\Delta S_{mic}$$

The results are tabulated in (Table 59-61), the values of $\Delta G_{mic}$ were always negative, indicating that the micellization process is a spontaneous one(212). Increasing the hydrophobic chain length, as well as the temperature, increased the negativity of $\Delta G_{mic}$. This occurred due to an increasing repulsion between water and the amphiphile molecules, which suppressed surfactant molecules for micellization to decrease the water/hydrophobe interaction(208). For that the triple chain Gemini surfactants showed the more negative $\Delta G_{mic}$ value.

$\Delta S_{mic}$ values decreased by increasing the hydrophobic chain length, indicating the restricted motion of the amphiphiles, which increased the ordering inside the micelles.

The negativity of $\Delta H_{mic}$ values showed the spontaneity of the micellization process, all positive indicating that the transfer of unimers from solution to the micelle is enthalpically unfavored endothermic process.

## (VI) Thermodynamic Parameters of Adsorption of Gemini Amphiphiles:

The thermodynamic parameter values of adsorption $\Delta G_{ads}$, $\Delta H_{ads}$ and $\Delta S_{ads}$ were calculated via the following equations, respectively(211) :

$$\Delta G_{ads} = \Delta G_{mic} - (0.6023 \times \pi_{cmc} \times A_{min}),$$

$$\Delta S_{ads} = \partial \Delta G_{ads} / \partial T \text{ and}$$

$$\Delta H_{ads} = \Delta G_{ads} + T \Delta S_{ads}$$

Analyzing the thermodynamic parameters of adsorption, the $\Delta G_{ads}$ values are all negative and more negative than $\Delta G_{mic}$, which refers to the higher tendency of these amphiphiles to adsorption at air–water interface rather than micellization (212). The triple chain gemini surfactants gave the lowest $\Delta G_{ads.}$

The values of $\Delta S_{ads}$ are all positive and greater than the values of $\Delta S_{mic}$ for the same compound. This may reflect the greater freedom of motion of the hydrophobic chains at the planer air–aqueous solution interface. These observations are consistent with data reported by others (213).

The values of $\Delta H_{ads}$ are all more positive than $\Delta H_{mic}$, leads to the process of adsorption at air/aqueous interface more than in the micellization process.

Table (56) : **Surface Parameters of *N*,*N*-bis(5-hydroxy-3,7-dioxa-alky)-alkenamide sulfates:**

| Compound No. | R | R̀ | T ($^{o}$C) | CMC (M) × $10^{-5}$ | $\gamma_{CMC}$ (dyn/cm) | $\pi_{cmc}$ (dyn/cm) | $\Gamma_{max}$ × $10^{-11}$ (mol/cm$^2$) | $A_{min}$ (A$^{o\ 2}$) |
|---|---|---|---|---|---|---|---|---|
| XXIIi | $C_{12}$ | $C_6$ | 30 | 7.0 | 33.5 | 38.5 | 3.1 | 532.1 |
| XXIIi | $C_{12}$ | $C_6$ | 40 | 7.3 | 33 | 39 | 2.9 | 570.6 |
| XXIIi | $C_{12}$ | $C_6$ | 50 | 7.7 | 31 | 41 | 2.7 | 610.4 |
| XXIIIi | $C_{14}$ | $C_6$ | 30 | 6.0 | 33 | 39 | 3.2 | 522.1 |
| XXIIIi | $C_{14}$ | $C_6$ | 40 | 6.2 | 31.5 | 40.5 | 3.1 | 533.9 |
| XXIIIi | $C_{14}$ | $C_6$ | 50 | 6.6 | 29.5 | 42.5 | 2.8 | 582.6 |
| XXIVi | $C_{18}$ | $C_6$ | 30 | 1.7 | 31 | 41 | 3.9 | 425.7 |
| XXIVi | $C_{18}$ | $C_6$ | 40 | 1.8 | 30 | 42 | 3.6 | 454.8 |
| XXIVi | $C_{18}$ | $C_6$ | 50 | 2.1 | 28.5 | 43.5 | 3.2 | 514.0 |

Table (57): **Surface Parameters of *N,N*-bis-(2-hydroxy-ethyl)- (2,5-dialkyl-[1,3]dioxolan-4-yl)-alkanamide sulfates:**

| Compound No. | R | Ŕ | T (°C) | CMC (M) × $10^{-4}$ | $\gamma_{CMC}$ (dyn/cm) | $\pi_{cmc}$ (dyn/cm) | $\Gamma_{max} \times 10^{-11}$ (mol/cm$^2$) | $A_{min}$ (A$^{o\,2}$) |
|---|---|---|---|---|---|---|---|---|
| XXXIVii | $C_{12}$ | $C_9$ | 30 | 4.5 | 35.5 | 36.5 | 2.6 | 631.3 |
| XXXIVii | $C_{12}$ | $C_9$ | 40 | 4.8 | 34 | 38 | 2.5 | 648.5 |
| XXXIVii | $C_{12}$ | $C_9$ | 50 | 5.3 | 32 | 40 | 2.3 | 700.5 |
| XXXVii | $C_{14}$ | $C_9$ | 30 | 3.4 | 31.5 | 40.5 | 3.0 | 553.4 |
| XXXVii | $C_{14}$ | $C_9$ | 40 | 3.7 | 30 | 42 | 2.67 | 621.8 |
| XXXVii | $C_{14}$ | $C_9$ | 50 | 4.1 | 28 | 44 | 2.5 | 664.1 |
| XXXVIii | $C_{18}$ | $C_9$ | 30 | 0.74 | 29.5 | 42.5 | 3.2 | 518.8 |
| XXXVIii | $C_{18}$ | $C_9$ | 40 | 0.75 | 28 | 44 | 3.0 | 544 |
| XXXVIii | $C_{18}$ | $C_9$ | 50 | 0.81 | 26 | 46 | 2.74 | 605.9 |

Table (58) : **Surface Parameters of 1,ω-bis(alkenoxy)-dihydroxy-dioxa-alkane sulfates:**

| Compound No. | R | R̀ | T ($^oC$) | CMC (M) × $10^{-4}$ | $\gamma_{CMC}$ (dyn/cm) | $\pi_{cmc}$ (dyn/cm) | $\Gamma_{max} \times 10^{-11}$ (mol/cm$^2$) | $A_{min}$ ($A^{o\,2}$) |
|---|---|---|---|---|---|---|---|---|
| XXXXVIi | $C_{12}$ | $C_2$ | 30 | 5.0 | 36 | 36 | 2.9 | 566.6 |
| XXXXVIi | $C_{12}$ | $C_2$ | 40 | 5.3 | 34 | 38 | 2.7 | 601.2 |
| XXXXVIi | $C_{12}$ | $C_2$ | 50 | 5.8 | 31.5 | 40.5 | 2.6 | 646.0 |
| XXXXVIIi | $C_{14}$ | $C_2$ | 30 | 3.1 | 35 | 37 | 3.0 | 559.0 |
| XXXXVIIi | $C_{14}$ | $C_2$ | 40 | 3.2 | 35 | 37 | 2.9 | 576.4 |
| XXXXVIIi | $C_{14}$ | $C_2$ | 50 | 3.5 | 32 | 40 | 2.6 | 628.9 |
| XXXXVIIIi | $C_{18}$ | $C_2$ | 30 | 0.62 | 30 | 42 | 3.4 | 488.8 |
| XXXXVIIIi | $C_{18}$ | $C_2$ | 40 | 0.63 | 29.5 | 42.5 | 3.1 | 527.0 |
| XXXXVIIIi | $C_{18}$ | $C_2$ | 50 | 0.66 | 28 | 44 | 2.9 | 564.7 |

Table (59) : **Thermodynamic Parameters of Micellization and Adsorption of *N,N*-bis(5-hydroxy-3,7-dioxa-alky)-alkenamide sulfates:**

| Compound No. | R | R̀ | $\Delta G_{mic}$ kJ.mol$^{-1}$ | $\Delta S_{mic}$ kJ.mol$^{-1}$.k$^{-1}$ | $\Delta H_{mic}$ kJ.mol$^{-1}$. | $\Delta G_{ads}$ kJ.mol$^{-1}$ | $\Delta S_{ads}$ kJ.mol$^{-1}$.k$^{-1}$ | $\Delta H_{ads}$ kJ.mol$^{-1}$. |
|---|---|---|---|---|---|---|---|---|
| **XXIIi** | $C_{12}$ | $C_6$ | **-23.38** | - | - | **-35.41** | - | - |
| **XXIIi** | $C_{12}$ | $C_6$ | **-24.45** | **0.107** | **+9.041** | **-37.85** | **0.214** | **+29.132** |
| **XXIIi** | $C_{12}$ | $C_6$ | **-25.09** | **0.102** | **-4.418** | **-40.16** | **0.231** | **+34.453** |
| **XXIIIii** | $C_{14}$ | $C_6$ | **-23.75** | - | - | **-36.01** | - | - |
| **XXIIIii** | $C_{14}$ | $C_6$ | **-24.87** | **0.089** | **+10.186** | **-37.89** | **0.161** | **+18.763** |
| **XXIIIii** | $C_{14}$ | $C_6$ | **-25.49** | **0.081** | **-5.464** | **-40.40** | **0.281** | **+40.673** |
| **XXIViii** | $C_{18}$ | $C_6$ | **-26.84** | - | - | **-37.35** | - | - |
| **XXIViii** | $C_{18}$ | $C_6$ | **-27.90** | **0.053** | **5.278** | **-39.40** | **0.205** | **+24.765** |
| **XXIViii** | $C_{18}$ | $C_6$ | **-28.53** | **0.0491** | **-8.181** | **-41.99** | **0.259** | **+41.667** |

Table (60): **Thermodynamic Parameters of Micellization and Adsorption of *N*,*N*-bis-(2-hydroxy-ethyl)- (2,5-dialkyl-[1,3]dioxolan-4-yl)-alkanamide sulfates:**

| Compound No. | R | R̀ | $\Delta G_{mic}$ kJ.mol$^{-1}$ | $\Delta S_{mic}$ kJ.mol$^{-1}$.k$^{-1}$ | $\Delta H_{mic}$ kJ.mol$^{-1}$. | $\Delta G_{ads}$ kJ.mol$^{-1}$ | $\Delta S_{ads}$ kJ.mol$^{-1}$.k$^{-1}$ | $\Delta H_{ads}$ kJ.mol$^{-1}$. |
|---|---|---|---|---|---|---|---|---|
| **XXXIVii** | $C_{12}$ | $C_9$ | **-18.83** | - | - | **-32.70** | - | - |
| **XXXIVii** | $C_{12}$ | $C_9$ | **-19.61** | **0.180** | **+4.804** | **-34.45** | **0.175** | **+20.325** |
| **XXXIVii** | $C_{12}$ | $C_9$ | **-19.98** | **0.164** | **-8.386** | **-36.85** | **0.240** | **+40.670** |
| **XXXVii** | $C_{14}$ | $C_9$ | **-19.51** | - | - | **-33.00** | - | - |
| **XXXVii** | $C_{14}$ | $C_9$ | **-20.28** | **0.143** | **+3.821** | **-36.00** | **0.300** | **+57.900** |
| **XXXVii** | $C_{14}$ | $C_9$ | **-20.66** | **0.132** | **-8.386** | **-38.25** | **0.225** | **+34.425** |
| **XXXVIii** | $C_{18}$ | $C_9$ | **-23.24** | - | - | **-36.52** | - | - |
| **XXXVIii** | $C_{18}$ | $C_9$ | **-24.38** | **0.123** | **+11.302** | **-38.80** | **0.228** | **+32.564** |
| **XXXVIii** | $C_{18}$ | $C_9$ | **-24.95** | **0.118** | **-6.539** | **-41.73** | **0.293** | **+42.900** |

Table (61) : **Thermodynamic Parameters of Micellization and Adsorption of 1,ω-bis(alkenoxy)-dihydroxy-dioxa-alkane sulfates:**

| **Compound No.** | **R** | **R̀** | $\Delta G_{mic}$ kJ.mol$^{-1}$ | $\Delta S_{mic}$ kJ.mol$^{-1}$.k$^{-1}$ | $\Delta H_{mic}$ kJ.mol$^{-1}$. | $\Delta G_{ads}$ kJ.mol$^{-1}$ | $\Delta S_{ads}$ kJ.mol$^{-1}$.k$^{-1}$ | $\Delta H_{ads}$ kJ.mol$^{-1}$. |
|---|---|---|---|---|---|---|---|---|
| **XXXXVIi** | $C_{12}$ | $C_2$ | **-18.57** | **-** | **-** | **-30.85** | **-** | **-** |
| **XXXXVIii** | $C_{12}$ | $C_2$ | **-19.36** | **0.121** | **+5.367** | **-33.11** | **0.226** | **+37.628** |
| **XXXXVIiii** | $C_{12}$ | $C_2$ | **-19.74** | **0.113** | **-7.466** | **-35.49** | **0.230** | **+41.334** |
| **XXXXVIIi** | $C_{14}$ | $C_2$ | **-19.74** | **-** | **-** | **-32.19** | **-** | **-** |
| **XXXXVIIii** | $C_{14}$ | $C_2$ | **-20.65** | **0.103** | **+7.833** | **-33.49** | **0.130** | **+37.200** |
| **XXXXVIIiii** | $C_{14}$ | $C_2$ | **-21.08** | **0.098** | **-7.191** | **-36.23** | **0.274** | **+52.272** |
| **XXXXVIIIi** | $C_{18}$ | $C_2$ | **-23.67** | **-** | **-** | **-35.98** | **-** | **-** |
| **XXXXVIIIii** | $C_{18}$ | $C_2$ | **-24.82** | **0.074** | **+11.175** | **-38.31** | **0.233** | **+34.619** |
| **XXXXVIIIiii** | $C_{18}$ | $C_2$ | **-25.49** | **0.069** | **-3.849** | **-40.45** | **0.214** | **+28.672** |