AIM OF WORK

The aim of the present work was to prepare different types of conventional and gemini surface active agents derived from alkenoic fatty acids. More specifically the aims are:

1- Preparation of new unsaturated fatty acids (3-dodecenoic, 3-tetradecenoic) from commercial fatty derivatives.
2- Reduction of the used fatty acids (3-dodecenoic, 3-tetradecenoic and 9-octadecenoic acid) to the corresponding fatty alcohols.
3- Preparation of conventional surfactants from the fatty acids and their derivatives.
4- Preparation of gemini surfactants with different alkyl chain and different hydrophilic groups.
5- Preparation of new gemini surfactants bearing 1,3-dioxolane ring.
6- Evaluation of all the prepared surfactants.
7- Examination of their biodegradability properties.
8- Determination of the thermodynamic parameters of some synthesized surfactants.
9- Application of the prepared compounds in some different fields of applications such as detergents emulsifiers and wetting agents.

SUMMARY

The thesis is organised into four main sections: Introduction, Experimental methods, Results and Discussion, and Conclusion. The introduction is a basic review of conventional and gemini surfactants, discussing definition, structures, preparation and properties of these surfactants, followed by some application of surfactants. The materials and methods section contains a brief summary of the experimental techniques used for this project, leaving the results and discussion section free for the presentation and interpretation of experimental results. The results and discussion sections concentrate on confirmation of the structure of the prepared surfactants and their surface active properties and biodegradability.

It includes the preparation of 3-alkenoic acid (3-dodecenoic and 3-tetradecenoic acids) by Knoevenagel condensation between long chain aldehydes (decanal and dodecanal) with malonic acid in the presence of triethylamine, the structure of the synthesized fatty acids was confirmed by using infrared and nuclear magnetic resonance spectra. These fatty acids with oleic acid were used to prepare different types of surfactants.

The result and discussion section include five parts:

Part (I): It deals with the synthesis and evaluation of nonionic surfactants (I_{a-c}- III_{a-c}) obtained from direct propenoxylation of the fatty acids (3-dodecenoic, 3-tetradecenoic acids and oleic acids) by propylene oxide (5,7and 10 mole) adduct, in the presence of KOH as catalyst. Another type of nonionic surfactant was prepared in this part from dihydroxy fatty acid methyl ester (IV_{a-c}-VI_{a-c}), which obtained from the conversion of fatty acids into methyl ester followed by hydroxylation

with acetic acid and hydrogen peroxide in the presence of concentrated H_2SO_4. Another type of anionic surfactants (VII_{a-c}-XII_{a-c}), were obtained by reacting of oxypropenoxylated compounds with chlorosulfonic acid followed by neutralization with NaOH. The surface active properties and biodegradability of these compounds were studied and their structures were confirmed by examination of their infrared and nuclear magnetic resonance spectra.

Part II: It concerned with the synthesis of triple chain gemini surfactants. Compounds with three long chain alkyl groups (XIII-XV)i-iii, were prepared by the reaction of *N*-(long chain acyl)diethanol amines diglycidyl ethers with long chain fatty alcohol (hexanol, octanol and decanol). The diglycidyl ethers were easily obtained from the corresponding N-acyldiethanolamines and epichlorohydrin under phase catalytic conditions using tetrabutyl ammonium bisulfate.

Three types of gemini surfactants were prepared from these triple chain compounds. A nonionic surfactants $(XVI\text{-}XVIIIi\text{-}iii)_{a-c}$, were prepared by propenoxylation of (XIII, XV)i-iii with different moles of propylene oxide (5, 10 and 15 moles). These nonionic gemini surfactants were sulphated by chlorosulfonic acid then neutralized with NaOH, to introduce an anionic groups have a propylene oxide units in their molecules (nonionic-anionic) $(XIX\text{-}XXIi\text{-}iii)_{a-c}$, these compounds have both surface properties of anionic and nonionic surfactants. Moreover bis(sulfate) types of gemini surfactants (XXII, XXIVi-iii) of the triple chain compounds were obtained by direct sulfation then neutralization.

All the prepared gemini surfactants were confirmed by spectral and elemental analysis for those anionic ones, and their surface active properties and biodegradability were investigated.

Part III: It deals with the synthesis of new gemini surfactants bearing 1,3-dioxolane ring, which consider as cleavable surfactants. These compounds were obtained from the condensation of different kinds of aldehyde (benzaldehyde, decanal and dodecanal) with vicinal dihydroxy *N*-acyldiethanolamine (3,4-dihydroxy *N*-dodecanyl-diethanolamine, 3,4-dihydroxy *N*-tetradecanyldiethanolamine or 9,10-dihydroxy *N*-octadecanyldiethanol-amine) in the presence of p-toluenesulfonic acid, to 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). These compounds were converted into three types of surfactants as in part (II).

The surface properties, biodegradability and the spectral data for the prepared surfactants were studied in this section.

Part IV: It includes the preparation of double chain gemini compounds with different spacer length (XXXVII-XXXIXi-iii), which prepared by the reaction of glycol diglycidyl ethers [prepared from the reaction of glycols (ethylene glycol, 1,4-butylene glycol and 1,6-hexylene glycol) with epichlorohydrin], with long chain fatty alcohols (3-dodecenol, 3-tetradecenol and 9- octadecenol) obtained from the reduction of corresponding alkenoic fatty acids methyl esters. These compounds were converted to surface active derivatives by propenoxylation, propenoxylation then sulfation or only sulfation. They were investigated by different spectral methods. The surface active properties and biodegradability were investigated. The effect of spacer chain length on the surfactant behaviour was studied.

Part V: It deals with the thermodynamic parameters of some prepared surfactants. Surfactants micellize in solution after a critical concentration (CMC) depends on their molecular structure and

environmental conditions. The concept of the CMC value is very useful and perhaps the most frequently measured and discussed micellar parameter. Through surface tension versus surfactant concentration curves, several surface and thermodynamic parameters are derived such as ΔG_{mic}, ΔG_{ads}, ΔS_{mic}, ΔS_{ads}, ΔH_{mic} and ΔH_{ads} . Thermodynamics of micellization and adsorption processes were discussed.

Finally, the conclusions reiterates the main results and makes a final comparison between conventional and gemini surfactants.

All compounds contains straight alkyl chain so they are more chemically biodegradable and destructible surfactants which have less polluting effect on the environment, and are good emulsifiers (specially the gemini types), so they can be used in many different industry fields.