



# MONOETHANOLAMIDE BASED NON-IONIC GEMINI SURFACTANTS FROM RENEWABLE SOURCES: SYNTHESIS, CHARACTERIZATION AND ANTICORROSION STUDY

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## ABSTRACT

The synthesis of novel non-ionic Gemini surfactants were carried out in two stages in the present research work. Initially ethanol amine was converted into fatty amides by using four different fatty acid namely lauric, myristic, palmitic and oleic acid followed by reaction with 1,2,7,8-diepoxyoctane to form targeted non-ionic Gemini surfactants. The structure of new synthesized Gemini surfactants were confirmed by using FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. Corrosion inhibition efficiency was determined by weight loss method for different concentration. The shapes of synthesized surfactants were determined by Scanning electron microscopy. SEM study of these surfactants revealed that particles are in spherical and distorted spherical in shape. The synthesized Gemini surfactants have good inhibition efficiency against carbon steel.

**KEYWORDS:** Gemini Surfactant, Spectroscopy Characterization, SEM, Anticorrosion Study

## 1. INTRODUCTION

Surfactants are amphiphilic molecule consisting of both hydrophilic and hydrophobic regions. These substances are known to play a vital role in many process of interest in both fundamental and applied sciences. Today, new surfactants should be milder, safer and efficient with a minimal impact on the environment. Environmental awareness and protection have led to the development of more environmentally benign surfactant. There is trend toward replacing petrochemicals sources by renewable raw materials. [1-2]

Gemini surfactants are a newer type of surfactants capable of forming self assemblies having two amphiphiles in molecules, chemically bonded through a spacer group. They are more surface active by order of magnitude than conventional surfactants. This newer type of surfactants has attracted considerable interest since it became evident that these compounds have a very low critical micelles concentration and much greater efficiency in reducing surface tension than expected. [3-6] Due to their high molecular weight, skin penetration of Gemini surfactant is expected to be low which is one of the desirable properties of a surfactant to be used in body care products such as soaps, shampoos and cosmetics. However, the main factor that has prevented the use of Gemini surfactants in practical applications is their higher cost. [7]

There are several research publications on Gemini surfactants and their potential applications. Aratani et al have synthesized Gemini surfactants from tartaric acid and studied properties. Anno

Wagenaar et al was synthesized non-ionic reduced-sugar based bola amphiphiles and Gemini surfactants with an  $\alpha,\omega$ -diamino-(oxa) alkyl spacer. Wenjian Zhang et al synthesized nonionic Gemini Surfactant Di-Glycerol 2, 9-Dihexyldecanedioate and studied the physico-chemical and performance properties. [8-10]

In order to make the use of Gemini surfactant cost effective, efficient and economically viable in wide variety of applications, Gemini surfactant are expected to be produced via a low cost synthetic mechanism. In the present research work, a new Gemini surfactant using monoethanolamine as hydrophilic head group and four different fatty acid namely oleic acid, palmitic acid, myristic acid and lauric acid as source of hydrophobic tail has been synthesized. Synthesis involved initial conversion of ethanolamine into fatty ethanolamides which were dimerised using 1,2,7,8-diepoxyoctane as spacer. The prepared non-ionic Gemini surfactants were characterized & anticorrosion behaviors were studied in details.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Materials and Equipment Setup

The necessary chemicals required for the experiment viz. lauric acid (99%), oleic acid (65-88%), palmitic acid (99%), myristic acid (99%), monoethanolamine (98%), methanol, chloroform, acetonitrile were purchased as per the required grades from S. D. fine chemicals, Mumbai. The 1,2,7,8-diepoxyoctane was purchased from sigma Aldrich. Infrared (IR) spectra were obtained by SHIMADZU FTIR 8400 in the 400-4000 cm<sup>-1</sup> range using KBr pellets. <sup>1</sup>H nuclear

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magnetic resonance ( $^1\text{H-NMR}$ ) and  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C-NMR}$ ) spectra were obtained with Bruker advanced 400 MHz NMR spectrophotometer

## 2.2 Experimental Methodology

### Step-1: Synthesis of fatty monoethanolamides from fatty acids and monoethanolamine

The experimental setup consisted of 500 ml three necked round bottom flask equipped with a motor stirrer, a thermometer and a condenser. Ethanolamine (12.50 gm, 0.20 mole) was reacted with four different fatty acids namely lauric acid (41.04 gm, 0.20 mole), oleic acid (47.0 gm, 0.166 mole), myristic acid (43 gm, 0.188 mol) and palmitic acid (45 gm, 0.187) at 140°C. An oil bath was used to maintain a constant temperature. The reaction mixture was stirred continuously up to 10 hrs.

### Step-2: Purification of fatty monoethanolamides

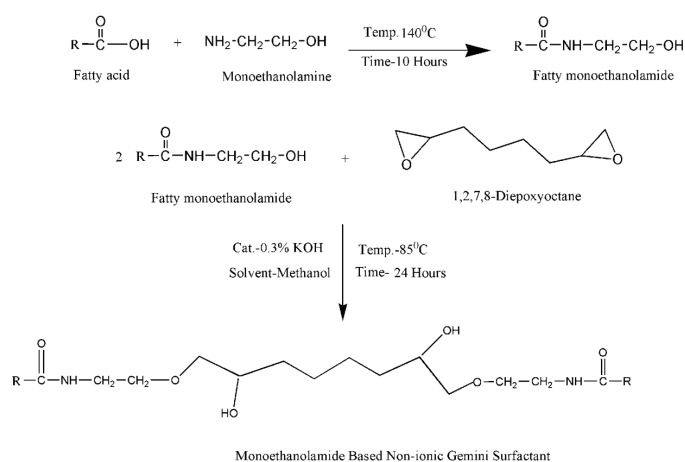
The reaction mixture was dissolved in a mixture of methanol and chloroforms solvents [50/50 (v/v)] and transfer into rotary evaporator. The solvent then eliminated by evaporation in a rotary evaporator. The resultant substance was the amide. Then acetonitrile solvent was added into the resultant amide and solution is cooled in ice bath. The acid remains soluble at this low temperature but the amide precipitated and subsequently recovered via filtration using what man's filter paper. [12]

### Product Analysis

The progress of reaction was monitored by analyzing the amount of unreacted fatty acid and amine in the reaction mixture by a titrimetric method such as acid value and amine value.

### Step-3: Synthesis of Gemini surfactant from fatty monoethanolamides and 1,2,7,8-diepoxyoctane.

Lauryl monoethanolamide (15 gm, 0.061 mole), oleyl monoethanolamide (15 gm, 0.046 mol), palmityl monoethanolamide amides (15 gm, 0.058 mole) and myristyl monoethanolamide amide (15 gm, 0.055 mol) were loaded in a reactor vessels and vessels are purged with nitrogen. The KOH (0.3% referred to the weight of the fatty ethanol amide) dissolved in the dry methanol is added into the reaction vessels and then temperature was raised to 85°C for 24 hours. The spacer 1,2,7,8-diepoxyoctane was then added drop wise in each vessels. The mole ratio of fatty ethanol amides and 1,2,7,8-diepoxyoctane was 2:1 respectively. The reaction was completed after two hour under the presence of nitrogen environment. [2] Synthesis of Gemini surfactant as shown in fig. 1.



$\text{R}_1 = \text{C}_{11}\text{H}_{23}$  [Lauryl monoethanolamide Based Gemini Surfactant (GSLMDO)],  $\text{R}_2 = \text{C}_{13}\text{H}_{27}$ , [Myristyl monoethanolamide Based Gemini Surfactant (GSMMDO)],  $\text{R}_3 = \text{C}_{15}\text{H}_{31}$ , [Palmityl monoethanolamide Based Gemini Surfactant (GSPMDO)],  $\text{R}_4 = \text{C}_{17}\text{H}_{33}$  [Oleyl monoethanolamide Based Gemini Surfactant (GSOMDO)]

**Figure 1: Synthesis of Gemini surfactant from fatty monoethanolamides and 1,2,7,8-diepoxyoctane**

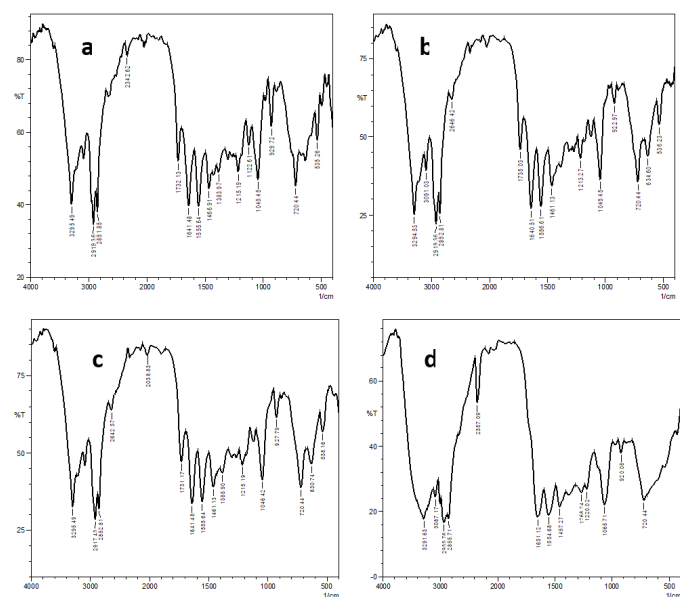
## 3. Result and Discussion

### 3.1 Characterization:

#### 3.1.1 FTIR Spectroscopy:

##### 3.1.1.1 FTIR spectra of fatty monoethanolamides

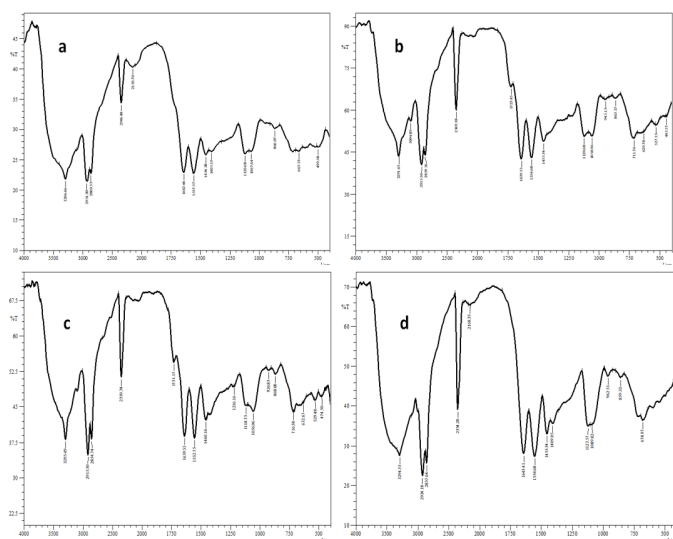
The FTIR spectra of lauryl monoethanolamides (a), myristyl monoethanolamides (b), palmityl monoethanolamides (c), oleyl monoethanolamides (d) assigned for observed peaks as shown in fig. 2. It shows absorption band at 1650  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching in amide), 2935  $\text{cm}^{-1}$  and 2852  $\text{cm}^{-1}$  ( $\text{C-H}$  asymmetric and symmetric stretching in methylene and methyl group), 3296- $\text{cm}^{-1}$  ( $\text{OH}$ - symmetric stretching), 1461  $\text{cm}^{-1}$  ( $\text{C-H}$  bending in methylene and methyl group), 720  $\text{cm}^{-1}$  ( $\text{CH}_2$ ) $_n$ -skeletal present in synthesized compound). [13]



**Figure 2: FTIR Spectra of lauryl monoethanolamides (a), myristyl monoethanolamides (b), palmityl monoethanolamides (c) and oleyl monoethanolamides (d).**

### 3.1.1.2 FTIR spectra of monoethanolamide based non-ionic Gemini surfactant

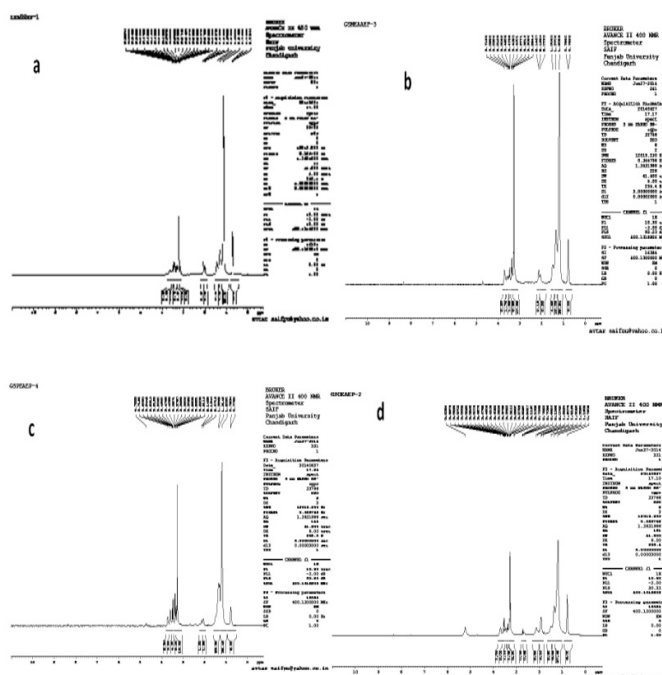
The FTIR spectra of Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c), GSOMDO (d) assigned for observed peaks as shown in fig. 3. It shows absorption bands at 1642 cm<sup>-1</sup> (C=O stretching in amide), 2935 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> (C-H asymmetric and symmetric stretching in methylene and methyl group), 1461 cm<sup>-1</sup> (C-H bending in methylene and methyl group), 1120-1045 cm<sup>-1</sup> (C-O stretching in C-O of ether), 3296 cm<sup>-1</sup> (OH-symmetric stretching), 3094 cm<sup>-1</sup> (N-H stretching in amide), 720 cm<sup>-1</sup> for  $-(CH_2)_n-$  skeletal present in synthesized compound). [13]



**Figure 3: FTIR spectra of synthesized ethanolamide based non-ionic Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c) & GSOMDO (d).**

### 3.1.2 <sup>1</sup>H-NMR spectra of monoethanolamide based non-ionic Gemini surfactants

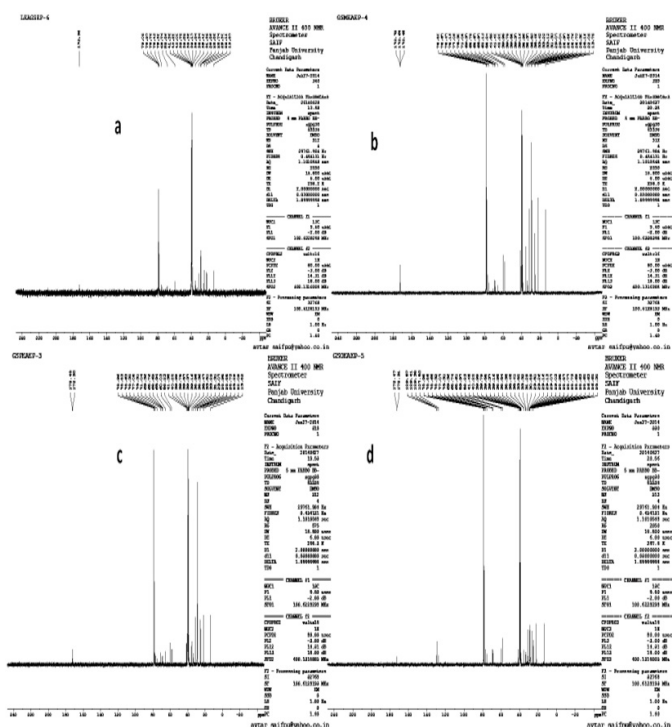
The <sup>1</sup>H-NMR spectra of Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c) GSOMDO (d) assigned for observed peaks as shown in fig. 4. The shift at 0.79 ppm and 1.3 ppm were due to the presence of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) group in synthesized compounds respectively. The multiplet accruing at 3.7 ppm to 3.4 ppm may be due to the proton present in ether group CH<sub>2</sub>-O-C. The proton with  $\delta$ -value at 1.5 ppm is due to the CH- proton present in the synthesized compounds. The proton with  $\delta$ -value at 4.7 ppm is due to the proton attached to oxygen atom in hydroxyl group (OH) in the synthesized compound. The proton in CH<sub>2</sub> group attached to NHCOR resonated at 3.3 ppm. The peak obtained at 8.3 ppm was due to the proton attached to N atom i.e. due to the NH moiety. [13] Some extra peaks were obtained. They resulted not only from the synthesized compounds but also from the other byproducts and unreacted compounds.



**Figure 4: <sup>1</sup>H-NMR spectra of synthesized ethanolamide based non-ionic Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c) & GSOMDO (d).**

### 3.1.3 <sup>13</sup>C-NMR spectra of monoethanolamide based non-ionic Gemini surfactants

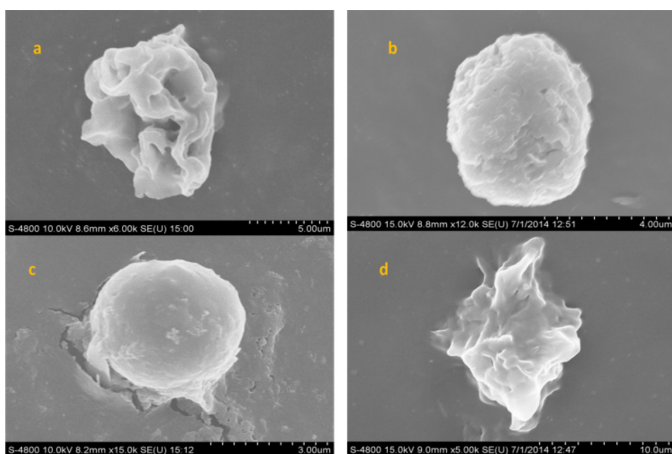
The <sup>13</sup>C-NMR spectra of Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c) GSOMDO (d) obtained for the observed peaks as shown in fig. 5. The chemical shift at 172 ppm may be assigned to the C=O of amide in the synthesized compound. The various peaks at 13-51 ppm were due to the presence of methyl and methylene group in synthesized compound. The chemical shift at 61 ppm may be assigned to RCH<sub>2</sub>OR i.e. ether group present in the synthesized compound. The peak accruing at 75 ppm was due to the presence of CH-OH moiety in the compound. The peak at 43 ppm may be assigned to the R-CH<sub>2</sub>-N group present in the synthesized surfactant. The presence of unsaturation in alkyl chains of GSOMDO was evident from the chemical shift at 127-129 ppm. [14]



**Figure 5: 13C-NMR spectra of synthesized ethanol amide based non-ionic Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c) & GSOMDO (d).**

**3.1.4 Scanning Electron Microscopy (SEM)**

SEM has been used to characterize the surface morphology of substances. The fig.6 (a), (b) (c), (d) shows the SEM image of the different synthesized surfactants in aqueous medium. It was observed that image of GSPMDO is the spherical in shape and other surfactant are distorted from spherical shape which may be due to the presence of different chain length in different surfactant molecule and other factor like solubilization of material, concentration, temperature and ionic strength. [3-5]



**Figure 6: SEM micrograph of ethanol amide based non-ionic Gemini surfactants GSLMDO (a), GSMMDO (b), GSPMDO (c) & GSOMDO (d).**

**3.2. Anticorrosion Study**

The inhibiting efficiency & corrosion rate of the prepared Gemini surfactants were determined by using weight-loss technique in 1N H2SO4 solution at 30°C.[15] This work was performed on carbon steel with composition: 1.47% C, 0.20% N, 0.27% O, 0.09% Na, 0.09% Mg, 0.08% Si, 0.05 Ca, 0.85% Fe. Rectangular specimens of C-steel with dimensions 1.0 cm x 1.0 cm x 0.07 cm were used.

Adsorption of the surfactant molecules onto metal surface is responsible for the corrosion inhibition of the metal which related to its capability of aggregate to form micelles. [16] Surfactants with low cmc values are good corrosion inhibitor, because they adsorb at low concentrations. Most acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms.[17-19] The value of corrosion rate (K) was calculated by using equation : [20]

$$K = \frac{W}{S t}$$

Where W is the average wt. loss of three parallel carbon steel sheets, S is the surface area of the specimen and t is the immersion time.

The degree of surface coverage (θ) and the percentages inhibition efficiency (ηw) were calculated using equations: [23]

$$\theta = 1 - W_o / W$$

$$\eta_w = (1 - W_o / W) \times 100$$

Where W is the weight loss of carbon steel in the absence of inhibitor and Wo is the weight loss of carbon steel in the presence of the inhibitor.

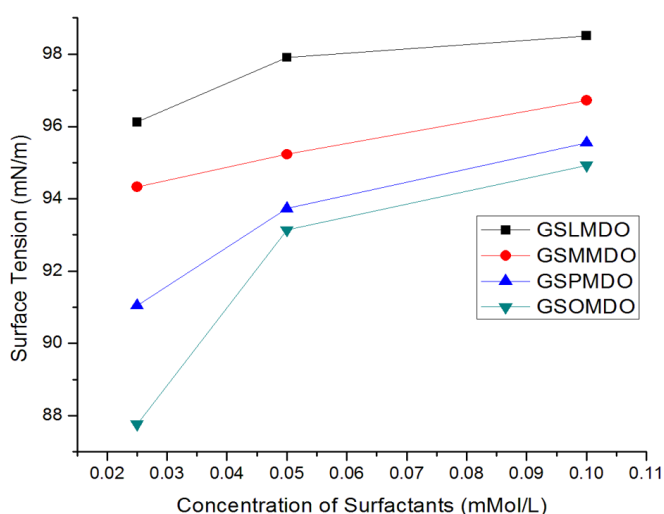
The value of corrosion rate (k), degree of surface coverage (θ) and percentage of inhibition efficiency (ηw) are listed in table 1.

Compound	Concentration of inhibitor (%)	Corrosion Rate (K)	Surface Coverage (θ)	Inhibition Efficiency (ηw %)
GSLMDO	0.1	1.488 X 10 <sup>-3</sup>	0.9850	98.5074
	0.05	2.0832 X 10 <sup>-3</sup>	0.9791	97.9104
	0.025	3.8688 X 10 <sup>-3</sup>	0.9611	96.1194
GSMMDO	0.1	3.2736 X 10 <sup>-3</sup>	0.9671	96.7164
	0.05	4.7616 X 10 <sup>-3</sup>	0.9522	95.2238
	0.025	5.6544 X 10 <sup>-3</sup>	0.9432	94.3283
GSPMDO	0.1	4.464 X 10 <sup>-3</sup>	0.9555	95.5522
	0.05	6.2496 X 10 <sup>-3</sup>	0.9373	93.7313
	0.025	8.928 X 10 <sup>-3</sup>	0.9104	91.044776
GSOMDO	0.1	5.0592 X 10 <sup>-3</sup>	0.9492	94.9253

	0.05	6.8448 X 10 <sup>-3</sup>	0.9313	93.1343
	0.025	0.0122 X 10 <sup>-3</sup>	0.87761	87.761

**Table 1: Weight loss result of carbon steel corrosion for different concentrations of the synthesized Gemini surfactants at 30°C in 1N H<sub>2</sub>SO<sub>4</sub> aqueous solution for 24 hrs.**

The obtained results indicated that inhibition efficiency increases with decreasing the number of repeated methylene group in the hydrophobic chain and increasing the concentration of synthesized surfactants. Plotting the inhibition efficiency versus concentration of synthesized surfactant at temperature at 30°C is illustrated in fig. 7. From this fig. it is clear that the inhibition efficiency increases with increasing concentration of inhibitor.



**Figure 7: The graph of inhibition efficiency against concentration of synthesized non-ionic Gemini surfactants at 30°C.**

#### 4. CONCLUSION

In the present research a new protocol for the synthesis of novel monoethanolamine based non-ionic Gemini surfactant through an environmental friendly process has been described. Effort has been made in to design and develop a new Gemini surfactant with improved surface properties. Non-ionic Gemini surfactants have wide applications because of their high surface activity and low critical micelle concentration. The four monoethanolamine based surfactants GSLMDO, GSMMDO, GSPMDO and GSOMDO has been successfully synthesized from four different fatty acid namely lauric, myristic, palmitic and oleic acid, monoethanolamine and 1,2,7,8-diepoxyoctane as spacer. The various functional groups present in synthesized surfactants are determined by FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The synthesized surfactants molecules are spherical and distorted spherical in shape. Synthesized surfactants have very good anticorrosion efficiency. They can be used as anticorrosion agents.

#### 5. ACKNOWLEDGMENT

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#### 6. REFERENCES

- Broze G. Handbook of surfactant, Surfactant science series, part A: Properties, 1st Ed., Marcel Dekker Inc: New York. 82; 1999:76-78.
- Brita MF, Krister H, Eva GK, Karin B. Fatty amide ethoxylates: synthesis and self assembly. Journal of Surfactant and Detergent. c4(2); 2001: 175-183.
- Hait SK, Moulik SP. Gemini surfactants: a distinct class of self-assembling molecules. Current Science. 82(9); 2012:1101-1111.
- Janardhan R, Vijayabaskar V, Reddy BSR. Synthesis and characterisation of sulfonated dimeric malenised soya fatty acid : A novel Gemini surfactant. J. Surface Sci. Technol. 28(3-4); 2012:163-178.
- Gawali IT, Usmani GA. Synthesis, characterization and some properties of glycerol ester based non-ionic gemini surfactant with 1, 2, 7, 8 -diepoxyoctane as spacer. International journal of science and research.3(10): 2014:580-584.
- Wenjian Z., Liguoz Z., Zhaoyun D. Synthesis and performance of nonionic Gemini surfactant di-glycerol 2, 9-dihexyldecane dioate. Journal of Dispersion Science and Technology. 30 (9); 2009:1161-1166.
- Adewale A, Andrea G, Thomas W. Properties of sodium phosphate hydroxy ethanolamide gemini surfactant synthesized from the seed oil of Luffa cylindrical. Central European Journal of Chemistry. 11(8); 2013:368-1380.
- Aratani K, Oida T, Shimizu T, Hayashu Y. Preparation and properties of Gemini surfactant from tartaric acid. communications presented as a las Jornadas del Comite Espanol de la Detergencia. 28; 1998: 45-46.
- Anno W, Engberts JBFN. Synthesis of nonionic reduced-sugar bola amphiphiles and surfactants with an  $\alpha,\omega$ -diamin-(oxa) alkyl spacer. Science Direct Tetrahedron. 63; 2007:10622-10629.
- Gawali IT, Usmani GA. Study of physico-chemical properties of glycerol ester based non-ionic gemini Surfactant. International Journal of Science and Research. 3(11); 2014:580-584
- Kandeel EM. Synthesis and performance of glycerol ester-based non-ionic surfactants. Der Chemica Sinica. 2 (3); 2011: 88-98.
- Thomas MS. Analysis of surfactant, second edition, BASF Corporation New York, Vol. 96. Detergent. 2001: 175-183.
- Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR. Vogel's text book of practical organic chemistry, Addison Wesley Longman, Inc, 1989:1413-1434.
- Harwood LM, Moody C J, Percy JM "Experimental Organic Chemistry, Standard and Microscale, second edition, Wiley Pvt. Ltd, India, 2011.
- Patial P, Shaheen A, Ahmad I. Synthesis, characterization and evaluation of the surface active properties of novel cationic imidazolium gemini surfactant. Journal of Surfactant & Detergent. 17(2); 2013: 253-260.
- Branzoi V, Branzoi F, Baibarac, M. The inhibition of the corrosion of Armco iron in HCl solutions in the presence of surfactants of the type of N-alkyl quaternary ammonium salts. Mater. Chem. Phys. 65 (3); 2010: 288-297.
- Xinkuai H, Yumei J, Chen L, Luye W. Inhibition properties and adsorption behaviour of imidazole and 2-phenyl-2-imidazoline on aa5052 in 1.0 m hcl solution. Corrosion Science. 83; 2014:124-136.
- Atkin R, Craig, VSJ, Wanless EJ, Biggs S. The influence of chain length and electrolyte on the adsorption kinetics of cationic surfactants at the silica-aqueous solution interface. Journal of

Colloid and Interface Science. 266(2):2003, 236-244.

19. Tang LB, Mu GN, Liu GH. The effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 m hydrochloric acid. Corrosion Science. Corros. Sci. 45; 2003: 2251-2262.
20. Manjula P, Manonmani S, Jayaram P, Rajendran S. Corrosion behaviour of carbon steel in the presence of N-cetyl-N,N,N-trimethylammoniumbromide, Zn and calcium gluconate. 48; 2001: 319-324.

## 7. Author Profile



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