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Synthesis, Characterization and Some Properties of Glycerol Ester Based Non-Ionic Gemini Surfactant with 1, 2, 7, 8 -Diepoxideoctane as Spacer

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Abstract: ***The synthesis of novel glycerol based non-ionic gemini surfactant was carried out in two stages in the present research work. Initially glycerol was esterified using cotton seed oil at higher temperature followed by reaction with 1, 2, 7, 8-Diepoxideoctane to form the non-ionic gemini surfactant. The new gemini surfactant was characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy and Scanning electron microscopy (SEM). The effect of surfactant on Solubilization of polar and non-polar solute was studied. Contact angles with respect to different solid probes were measured. It can be concluded that the new glycerol-based non-ionic gemini surfactant exhibit generally good solubilizing and wetting behaviour.***

Keywords: Gemini Surfactant, Characterization, SEM, Solubilization Behaviour, Contact angle.

1. Introduction

Surfactants are well known materials generally described as compounds bearing a hydrophobic and hydrophilic group per molecule. They are well known to have numerous uses such as emulsifier, detergents, dispersants and solubilizing agents in the field of cosmetic, textile treatment, industrial and personal cleaning operation. As consequence of hydrophobic effect, the surfactants within the aggregated assemblies are oriented with their polar head groups to the aqueous phase and their hydrophobic tail away from the aqueous phase [1]. 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 by renewable raw materials [2].

Gemini surfactants are 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. They have good water solubility and their ability to form micelles and lowering surface tension characteristics are fairly good as compared to conventional surfactants [1], [3]-[4]. Gemini surfactants have a very high potential for practical applications because of their excellent ability to reduce surface tension of water and low Krafft temperatures. 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 [5], [4].

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 Wagennaar et al synthesized non-ionic reduced-sugar based bola amphiphiles and gemini surfactants with an α, ω-diamino-(oxa) alkyl spacer. Wenjian Zhang et al synthesized non-ionic gemini surfactant Di-Glycerol 2, 9-Dihexyldecanedioate and studied the physico-chemical and performance properties [1], [6]-[7].

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. One of the keys of achieving this is by use of cheap and readily available feed stock and simple reaction mechanism. In the present research work, a new Gemini surfactant using glycerol as hydrophilic head group and cotton seed oil as source of hydrophobic tail has been synthesized. There is industrial important for the use of glycerol due to its low cost factor. Cotton seed oil contains linoleic acid as a major component. Pure linoleic acid is not cost effective and may not be economic for the industrial use. Synthesis involved initial esterification of glycerol to form glycerol ester which was dimerised using 1, 2,7, 8-Diepoxide. The prepared non-ionic Gemini surfactant was thoroughly characterized. Solubilization behaviour and contact angle measurement were studied in detail.

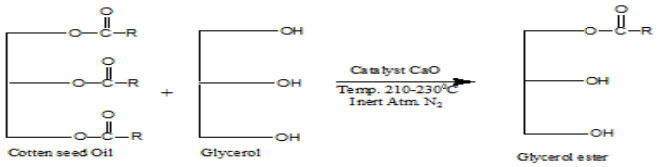
2. Experimental Procedure

2.1 Materials and Equipment Setup

The cotton seed oil was procured from local market. Glycerol with purity > 99%, Calcium oxide, 1, 2 7, 8-diepoxideoctane, Methanol, Sodium hydroxide were purchased from Merck. The Infrared (IR) spectrum was obtained by SHIMADZU FTIR 8400 in the 400-4000 cm^{-1} range using KBr pellets. Proton nuclear magnetic resonance (^{1}H –NMR) and ^{13}C nuclear magnetic resonance (^{13}C–NMR) spectra were obtained with Bruker advanced 400 MHz spectroscopy.

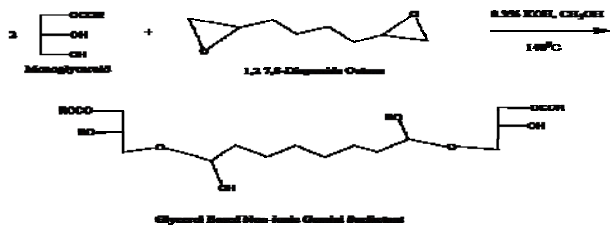
2.2 Experimental Section

Step1**:** The experimental set up consisted of a 250 ml three necked round bottom flask equipped with motor stirrer, a thermometer and condenser. The cotton seed oil (90 gm, 0.1 moles) was reacted with glycerol (23gm, 0.25 moles) by using calcium oxide (1% of total amount of oil) as catalyst. Firstly, the catalyst was dispersed in the oil. Then reaction mixture was heated to 80^{O}C for half an hour and temperature was increased to 210-230^{O}C. The reaction was continued for three hours in the inert atmosphere under the presence of nitrogen. The oil bath was used to maintain the constant temperature. The formation of glycerol ester was analyzed by using solubility test in methanol [8].



Scheme 1: Synthesis of Glycerol ester from cotton seed oil

Step 2: Glycerol ester 0.1 mole (31.2 gm) was charged in a 500 ml three necked round bottom flask. Then the temperature was raised to 85^{0}C and KOH (0.3% referred to the weight of the glycerol ester) dissolved in the dry methanol was added into the flask. The temperature was raised to 140^{0}C. The spacer 1, 2, 7, 8-diepoxideoctane 0.05 mole (7.1 gm) was then added drop wise for half an hour. The reaction was continued for three hours in the inert atmosphere under the presence of nitrogen. [9].



Scheme 2: Synthesis of Gemini surfactant from glycerol ester and 1, 2, 7, 8-Diepoxideoctane

3. Results and Discussion

3.1 Characterization

3.1.1 FTIR

IR spectra of Gemini surfactant is given in fig. 1. It shows absorption bands at 1734 cm^{-1} (C=O stretching), 2928 cm^{-1}and 2857 cm^{-1} (C-H asymmetric and symmetric stretching in methylene and methyl group), 1459cm^{-1} (O-H bending), 1109-1050cm^{-1} (C-O stretching in C-O of ether), 3414 cm^{-1} (OH- symmetric stretching), 715 cm^{-1} for -(CH$_2$)n-skeletal present in synthesized compound [10]

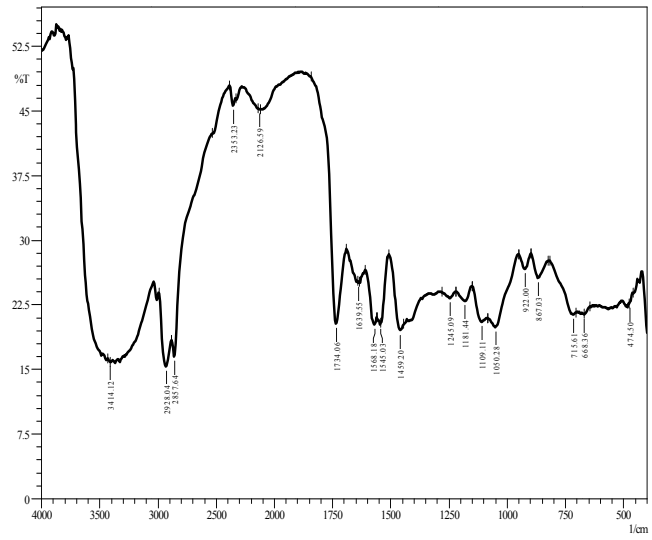


Figure 1: FTIR spectra of synthesized non-ionic Gemini surfactant

3.1.2 ^{1}H-NMR

The ^{1}H-NMR spectra of gemini surfactant assigned for observed peaks is shown in fig. 2. The shift at 0.9 ppm and 1.3 ppm are due to the presence of methyl (CH_3) and methylene (CH_2) group in synthesized compound respectively. The multiplet accruing at 3.7 ppm to 3.4 ppm may be due to the ether group i.e. CH_2-O-C group present in the synthesized compound. The proton with δ-value at 1.5 ppm is due to the CH- proton in the compound. The proton with δ-value at 5.5 ppm is due to the proton attached to oxygen atom i.e. presence of the hydroxyl group (OH) in the synthesized compound. The δ-value at 2.1 ppm is assigned to the ester group i.e. CH-CO-OR [10]. Some extra peaks are obtained. They resulted not only from the synthesized compound but also from other byproducts and unreacted compounds.

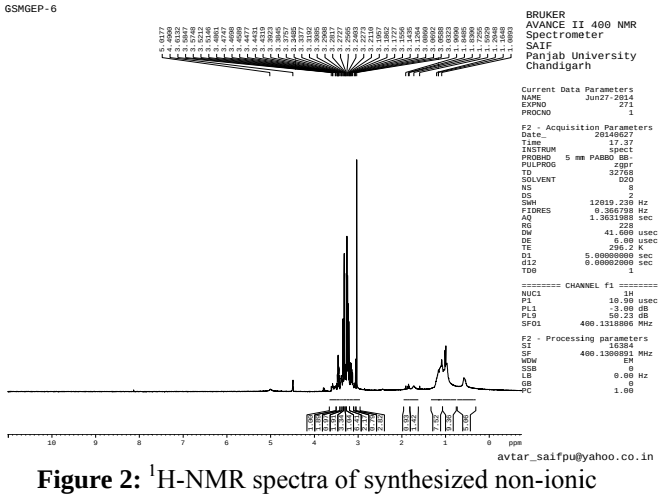


Figure 2: ^{1}H-NMR spectra of synthesized non-ionic gemini surfactant

3.1.3 ^{13}C-NMR

The ^{13}C-NMR spectra of gemini surfactant obtained for the observed peaks is shown in fig. 3. The chemical shift at 172 ppm may be assigned to the C=O of ester in the synthesized compound. The various peaks at 13-51 ppm

are due to the presence of methyl and methylene group in synthesized compound. The chemical shift at 63 ppm may be assigned to the RCH_2OR i.e. ether group present in the compound. The peak accruing at 71 ppm is due to the presence of CH-OH moiety in the compound. The small amount of unsaturated alkyl chains is evident from the line at 127-129 ppm [11].

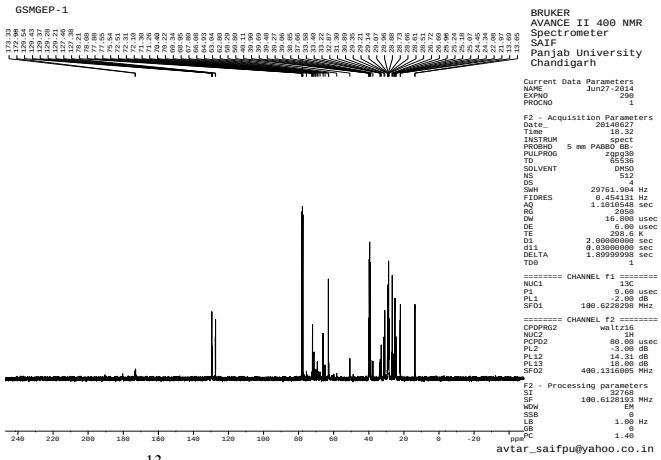


Figure 3: ^{13}C-NMR of synthesized non-ionic gemini surfactant

3.1.4 Scanning Electron Microscopy

SEM has been used to characterize the surface morphology of substances**.** Fig.4 shows the SEM image of the synthesized surfactant at different size in aqueous medium. It was observed that image of GSMGEP is somewhat spherical in shape. The shape of surfactant depends upon chain length of hydrophobic group, concentration, temperature and ionic strength [4].

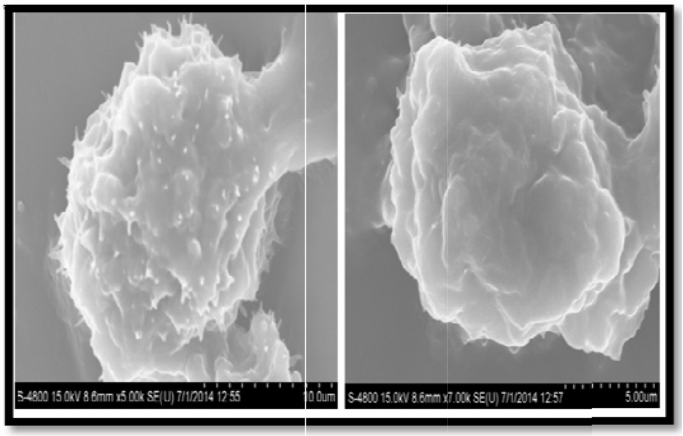


Figure 4: SEM image of synthesized non-ionic gemini Surfactants in aqueous solution

3.2. Solubilization Measurements [11]

A light-scattering technique was used to measure the solubilizing power of the prepared surfactant solutions at 28^{O}C using Hatch model 1/100 turbidity meter. Solubilizing power of surfactant solutions were measured using dispersing paraffin oil as a non-polar solute and 1-octanol as a polar solute. 1 gm of solute was mixed together with 100 ml of surfactant solution (1%) using rotary shaker at 240 rpm for different time interval (0, 2, 5, 10, 20, 30, 40, 50 and 60 minute) and turbidity was measured.

Solubilization behavior of aqueous solution of non-ionic Gemini surfactant is represented in fig.5 (a) and (b) for different type of solutes (paraffin oil and Heptanol as polar and a non-polar solute respectively) at 28^{O}C. These figures show that the turbidity of the surfactant solutions was low at the beginning of the experiment (T= 0) but that the turbidity of the system gradually increases with shaking time. The solubilizing process depends on many variables especially the nature of the solvent, alkyl chain length, head groups, concentration of solvent in solution and chemical structure of the solute.

3.3.1 Surfactant/paraffin oil system

Solubilizing power of synthesized Gemini surfactant for paraffin oil system is quite good as shown in fig.5 (a). This can be attributed to the fact that the amount of material solubilised increased with an increase in the size of the micelles. Hence any factor that causes an increase in either the diameter of the micelle or its aggregation number results in the increase of solubilization.

3. 3. 2 Surfactant/Heptanol solubilizing system

The Solubilization behavior for the surfactant /Heptanol system is shown in the fig.5 (b). The Solubilization behavior for the surfactant/Heptanol system is poorer than the behavior of the surfactant/paraffin oil system. This poor solubilization behavior indicates that emulsification is not the only interaction that took place between system components, but some other factor influence the Solubilization process. This factor could have been an interaction between the two polar head in the different molecules.

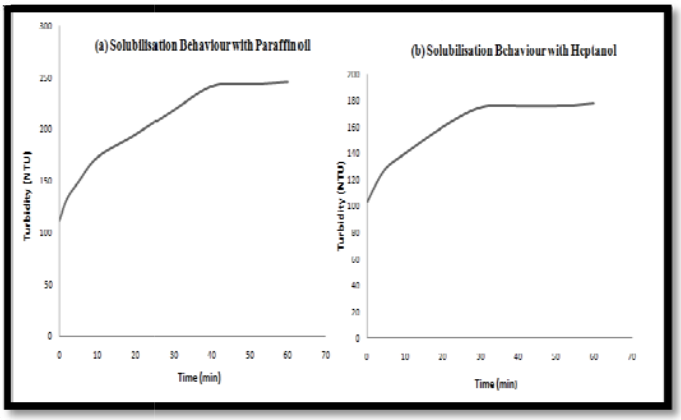


Figure 5: (a), (b) Solubilization behavior of the non-polar (light paraffin oil) and polar (heptanol) solvent in an aqueous surfactant solution (0.5%) at 28^{O}C

3.3 Contact Angle Measurement [13]

The dynamic contact angles of glass slides, steel slides, teflon slides against diluted surfactant solution (1mMol/L) were determined as shown in table 1. These values of contact angle were lower for steel and teflon than those obtained for pure water but higher for glass probes.

Smaller the contact angle better is the wetting power. These value shows that synthesized gemini surfactant has good wetting property for steel and Teflon but not for glass at concentration (1mMol/L).

Table 1: Contact angle measurement of synthesized (1mMol/L) non-ionic Gemini surfactant with respect to different solid probes.

Sr. No.	*Solid probes*	*Contact angle With respect to*	
		Distilled water	Surfactant sol (1mMol/L)
1	Glass	30^0	43^0
2	Steel	75^0	65^0
3	Teflon	98^0	85^0

4. Conclusion

In the present study a new protocol for the synthesis of novel glycerol based non-ionic Gemini surfactant through an environmental friendly process has been described. Non-ionic Gemini surfactants have wide applications because of their high surface activity and low critical micelle concentration. They can be used as emulsifier, dispersants, hydrophobic agent and also act as mild surfactant. Glycerol based nonionic Gemini surfactant was successfully synthesized by using, 1, 2 7, 8-Diepoxideoctane as spacer. The various functional groups present in the surfactant are determined by FTIR spectroscopy. The number of hydrogen atom and carbon atom of synthesized non-ionic gemini surfactant is also assigned by ^{1}H-NMR and ^{13}C-NMR spectroscopy. SEM analysis shows surface morphology of synthesized surfactant in aqueous solution is somewhat spherical in shape. The performance properties like solubilizing behaviour, Contact angle were studied. It can be concluded that the new glycerol-based non-ionic Gemini surfactant exhibit generally good solubilizing and wetting behaviour.

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References

[1] Wenjian Zhang, Liguo Zhou, and Zhaoyun Ding, “Synthesis and Performance of Nonionic Gemini Surfactant Di-Glycerol 2, 9-Dihexyldecanedioate”, Journal of Dispersion Science and Technology, vol. 30(9), pp. 1161-1166, 2009.
[2] Brita M. Folmer, Krister Holmeberg, Eva Gottberg klingskog and Karin bergstrom, “Fatty amide ethoxylates: synthesis and self assembly”, Journal of surfactant and detergent, vol. 4, pp. 175-183, 2001.
[3] R. Janardhan, V. Vijayabaskar & B. S. R. Redd, “Synthesis and Characterization of Sulfonated Dimeric Malenised Soya Fatty Acid: A Novel Gemini Surfactant”, Journal Surface Sci. Technol., vol. 28 (3-4), pp. 163-178, 2012.
[4] S. K. Hait and S. P. Moulik, “Gemini surfactants: A distinct class of self-assembling molecules”, Current Science, vol. 82(9), pp. 1101-1111, 2012.
[5] Adewale Adewuy, Andrea Gopfert, Thomas Wolff, “Properties of sodium phosphate-hydroxy ethanolamide gemini surfactant synthesized from the seed oil of Luffa cylindrical”, Central Europian Journal of chemistry, vol. 11(8), pp. 1368-1380, 2013.
[6] Aratani K., Oida T., Shimizu T., and Hayashu Y., “Preparation and Properties of gemini surfactant from tartaric acid”, Communications presented as a las Jornadas del Comite Espanol de la Detergencia, vol. 28, pp. 45-46, 1998.
[7] Anno Wagenaar & Jan B. F. N. Engberts, “Synthesis of nonionic reduced-sugar bola amphiphiles and surfactants with an α,ω-diamin-(oxa) alkyl spacer”, Science Direct Tetrahedron vol. 63, pp. 10622-10629, 2007.
[8] Wim D. Bossaert, Dirk E. De Vos, Wim M. Van Rhijn, Joren Bullen, Piet J. Grobet and Pierre A. Jacob, “Mesoporous Sulfonic Acids as Selective Heterogeneous Catalysts for the synthesis of Monoglyceride”, Journal of Catalysis, vol. 182(1), pp. 156-164,1999.
[9] Thomas M. Schmitt, second edition, “Analysis of surfactant”, BASF Corporation New York, Detergent, vol. 96 (2), 2001.
[10] B. S. Furniss, A. J. Hannaford , P. W. G. Smith, Austin R. Tatchell, “ Vogel’s Text book of practical organic chemistry, “Addision Wesley Longman, Inc. 1989.
[11] L. M. Harwood, C. J. Moody and J. M. Percy, second edition, “Experimental Organic Chemistry, Standard and micro scale”, Wiley Pvt. Ltd , India 2011.
[12] A. S. Mohamed, M. Z. Mohamad & D. A. Ismail, “Alinine-Based Surfactants: Synthesis and Some Surface Properties”, Journal of Surfactant, vol. 7 (4), pp. 415-419, 2004.
[13] Erwin A. Vogler, “Practical Use of Concentration-Dependent Contact Angles as a Measure of Solid-Liquid Adsorption. 1. Theoretical Aspects”, American Chemical Society, vol. 8 (8), pp. 2005-2012, 1992.
[14] E. M. Kandeel “Synthesis and Performance of Glycerol Ester-Based Non-ionic Surfactant”, Der Chemical Sinica, vol. 2 (3), pp. 88-98, 2011

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