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Synthesis and Characterisation of Sulfonated Dimeric Malenised Soya Fatty Acid : A Novel Gemini Surfactant

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Abstract — Gemini surfactants are a new type of surfactants that possess two hydrophilic heads and two hydrophobic tails bonded through a spacer group. The synthesis of a novel gemini surfactant was carried out in three stages in the present research. Initially soya fatty acid was malenised using maleic anhydride at higher temperature to avoid Diels Alder adduct, followed by the esterification with 1,4 butanediol to form the dimer. The dimer was sulfonated using sodium bisulfite. The new compound was characterised by chemical analyses, FT-IR spectra, ¹H NMR and supported by LCMS. Spectral data provide strong evidence for the formation of the gemini surfactant. The surfactant properties such as surface tension, critical micelle concentration, foam stability and contact angle were measured. Gemini surfactant was superior in surface active properties to the monomeric surfactant with one hydrophilic head and one hydrophobic tail. In particular, gemini surfactant had remarkably low critical micelle concentration.

Keywords : *Surfactant, gemini, malenisation, surfactant activity, soya fatty acid, -ene reaction, critical micelle concentration*

INTRODUCTION

Surfactants are amphiphilic molecules that are capable of undergoing self-assembly into aggregated systems [1]. These unique molecules generally consist of a polar head group and one or two hydrophobic tail(s). As a consequence of the hydrophobic effect,

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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.

Gemini surfactants are a newer type of classical surfactants and capable of forming self assemblies having two amphiphiles in a molecule chemically bonded through a spacer group [2]. (Fig. 1 – ref. www.acswebcontent.acs.org). They could be more surface active by order of magnitude than conventional surfactants [3]. They have good water solubility and their ability to form micelles and lowering surface tension characteristics are fairly good as compared to conventional surfactants [4].

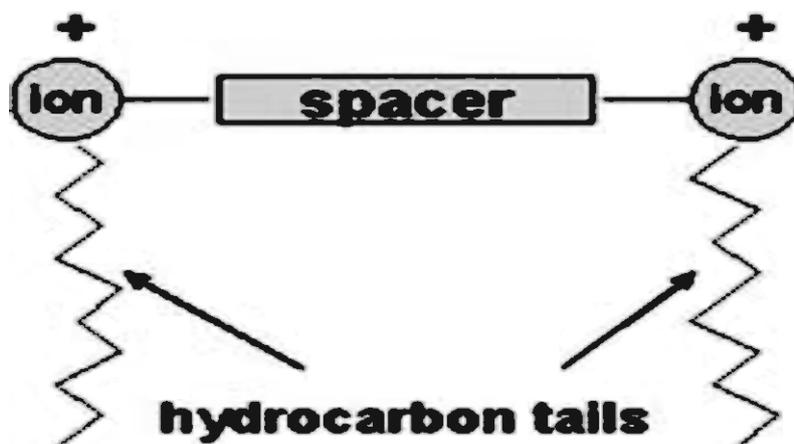


Fig. 1. Structure of a gemini surfactant.

They have excellent lime soap dispersing ability (LSDA) too [4]. Changes in the molecular structure and type to improve upon their properties have attracted the attention of chemists [5–8]. Conventional surfactant has a single hydrophobic tail connected to an ionic or polar head group, whereas a gemini has in sequence of a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail. This newer type of surfactants has attracted considerable interest since it became evident that these compounds have a very low critical micelle concentration and much greater efficiency in reducing surface tension than expected [3].

There are several research publications [9–19] on gemini surfactants and their potential applications. A non-ionic gemini surfactant [20] with sugar [21] as hydrophilic head and long chain alkyl group as hydrophobic tail, bonded by a short alkyl chain as the spacer was reported. A quite no. of nonionic surfactant species [22–23] with ethoxylate head and long chain lower alkyl or alkene were also reported. There are

further more surfactants reported on sulfate, phosphate and carboxylates of a secondary hydroxyl group [8,17–19], ethoxylated cotton seed oil alkylamide [24] and 1-Octadecanol [25].

There is a need to develop new, efficient and cost effective surfactants for suitable industrial applications. Efforts have been made in the present work to design and develop a new class of gemini surfactants, which has not been reported earlier. In the present research, we have synthesized a new gemini surfactant using soya fatty acid as a base, without any further purification. There is an industrial importance for the use of soya fatty acid due to its low cost factor. Soya fatty acid contains 47.2% of linoleic acid as a major component. Pure linoleic acid is not cost effective and may not be required for the industrial use. In soya fatty acid, the component linoleic acid is only reacting during the synthesis as –ene reaction and yielding the final surfactant. Synthesis involved initial malenization of soya fatty acid, which was dimerised using 1,4-butane diol. The prepared malenised gemini surfactant was sulfonated using sodium bisulfite as a sulphonating agent. The intermediates were characterised and the surfactant properties were investigated in detail.

EXPERIMENTAL

Materials :

Soya fatty acid-Industrial grade (Acid value : 199, saponification value : 200, iodine value : 125, freezing point 25°C, % oleic : 30.4, % linoleic : 47.2, % linoleinic : 2.3, % palmitic : 14.1, % stearic : 4.2 and % other fatty acids 2.0) procured from M/s Versatile Chemicals Limited, Mumbai, India used for the study. Other chemicals such as maleic anhydride, para toluene sulphonic acid, 1,4-butane diol, sodium bisulfite and isopropyl alcohol were of LR grade. All the materials were used without any further purification.

Methods :

Stage I : Synthesis of malenised soya (MS) —

93.3 g (0.33 mole) of soya fatty acid was heated for 1 h at 150°C under nitrogen, followed by the addition of 49 g (0.5 mole) of maleic anhydride and 1.4 g of para toluene sulphonic acid. The reactants were maintained at $205 \pm 5^\circ\text{C}$ for 5 h. The drop in the acid value of the soya fatty acid was checked for ascertaining the reaction completion.

Stage II : Synthesis of dimer of malenised soya (DMS) —

Malenised soya obtained from stage I was cooled to 120°C and added with 1.6 g of para toluene sulphonic acid. 15 g (0.17 mole) of 1,4-butane diol was added slowly

in 5 instalments, of 3 g each. The esterification reaction was carried out at 120°C for 3 h. The drop in the acid value of the malenised soya was checked for ascertaining the reaction completion. 36 ml of xylene was added in a Dean & Stark apparatus. Water formed during the reaction was removed by refluxion in the Dean & Stark apparatus.

Stage III : Sulfonated dimeric maleised soya (SDMS) —

The dimeric ester obtained from stage II was cooled to 90°C. 57.5 g (0.55 mole) of sodium bisulfite dissolved in 77.5 g of water and 15 g of isopropyl alcohol was added. The reaction was continued at 90°C for 3 h. % Water content, pH and %SO₃ were analysed.

The synthesis was followed by chemical methods such as acid value, % water content, % SO₃ and pH. Acid value and % water content were carried out as per IS : 548 : 1964 [26]. % SO₃ measured as a volumetric cationic titration against standard hyamine (benzethonium chloride), using methylene blue as the indicator [27].

pH was measured using precalibrated standard LAB INDIA make pH meter. FT-IR spectrum was taken using KBr pellet on BRUKER, IFS, 66V FT-IR spectrometer. ¹H NMR spectrum was taken using CDCl₃ as a solvent using JEOL GSX 400, NB FT NMR spectrophotometer. Molecular weight was calculated using Liquid Chromatography-Mass Spectra, Waters micromass quattro micro API model by mode APCI negative and direct infusion method.

Surface tension and critical micelle concentration (CMC) were determined using KRUSS tensiometer K100 (KRUSS GmbH, Hamburg) at ambient temperature by ring balance method [28]. Foaming power was determined using Ross-Miles pour-foam apparatus [29]. Contact angles were determined using KRUSS tensiometer K 100 by sorption measurements according to the Washburn method [30].

RESULTS AND DISCUSSION

Reaction Mechanism :

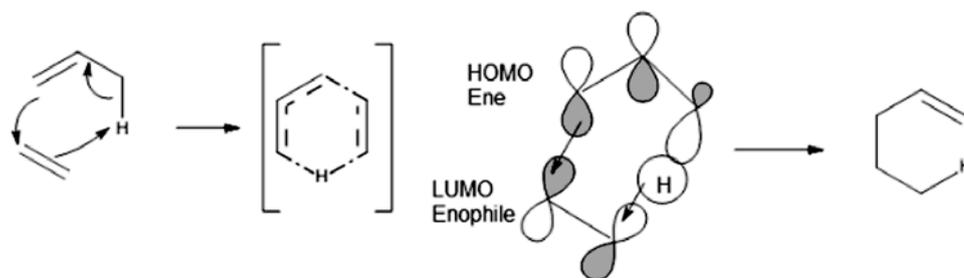
Linoleic acid component of soya fatty acid, which is non-conjugated and unsaturated, reacted with maleic anhydride at 205 ± 5°C to yield malenised soya. Chemical reaction occurs between the double bond of maleic group and the non-conjugated double bond of the linoleic acid.

The reaction followed an -ene synthesis mechanism by hydrogen abstraction between the maleic anhydride moiety and the carbon atom in the fatty acid chain. The -ene synthesis [31] resulted in the movement of the double bond of the fatty

acid chain to a conjugated double bond system, and the double bond carbon of maleic anhydride gets attached to the former non-conjugated double bond carbon of linoleic acid. This resulted in the formation of a single bond adjacent to the newly formed conjugated double bond in linoleic acid.

The -ene synthesis followed a pericyclic [32] reaction through the overlapping of orbitals of the reactants. Non-conjugated double bond of linoleic acid promoted a stable conjugated double bond structure in the fatty acid chain. It was happened though -ene reaction along with hydrogen abstraction. The reaction occurred at $205 \pm 5^\circ\text{C}$ which helped for the elimination of Diels-Alder adduct.

Soya Fatty acid was found to contain 30.4% oleic acid and 47.2% linoleic acid. As per the orbital conservation principle, oleic acid cannot undergo cycloaddition involving $2\pi + 2\pi$ orbitals with maleic anhydride under thermal condition. Linoleic acid with two unconjugated double bonds (i.e 1,4 diene) will not undergo Diels Alder reaction with maleic anhydride. It will undergo -ene syntheis, which is a cycloaddition of $2s + 2\pi + 2\pi$ orbitals involving HOMO (Highest Occupied Molecular Orbital) and the allylic part of linoleicacid with LUMO (Lowest Unoccupied Molecular Orbital) of maleic anhydride to form the product. The Scheme 1.0 illustrates a similar -ene reaction of ethylene with propylene.



Scheme 1.0 : Reaction mechanism of -ene reaction of ethylene with propylene type similar to the -ene synthesis of SDMS.

Analytical Characterisation :

The preparation of the gemini surfactant was carried out in three stages. During the first and second stages, acid values were determined till it remained constant. In the first stage, acid value during the first hour was 305, and after 3 and 5 hours, the same were 272 and 270 respectively. During the second stage, acid values after 1,

2 and 3 hours were 157, 146 and 144 respectively. After the third stage, the final sample was found to contain 61.0% water, pH of 7.4 and %SO₃ on 100% basis as 2.6.

FTIR Characterisation :

From the IR spectra of SDMS (Fig. 2), it was observed that the presence of carboxyl groups with H- bonding and carbonyl frequencies [33] of the ester, at 3436 cm⁻¹ and 1736 cm⁻¹ respectively. The asymmetric stretching of the ester was indicated at 1197 cm⁻¹. Assymmetric C-H stretch and symmetric C-H stretch of CH₃ of Soya fatty acid occurred 2925 and 2853 cm⁻¹ respectively. Malenization resulted in the formation of conjugation through the migration of double bond in the fatty acid chain and was ascertained by frequencies at 1574 cm⁻¹ for conjugated -C=C- stretch and 976 cm⁻¹ for -C=CH- deformation. The frequency at 1045 cm⁻¹ was due to the symmetric

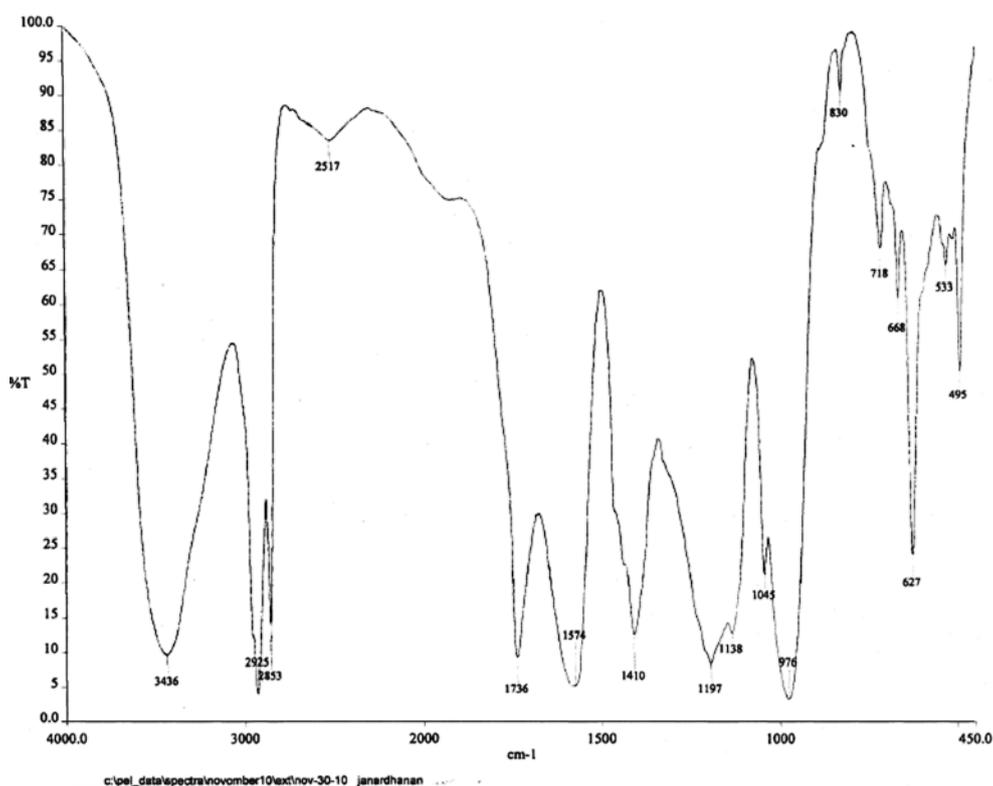


Fig. 2. IR of SDMS.

stretching of $-\text{SO}_3$ group. The formation of ester linkage and sulfonic salts in the final compound was confirmed unambiguously from the IR data.

^1H NMR Characterisation :

The ^1H NMR spectra of MS (Fig. 3) and SDMS (Figs. 4 (a) and (b)) were assigned for observed peaks [34]. The shift at 0.8 ppm and 1.5 ppm as in Fig. 3 were due to the presence of the methylene protons of soya fatty acid, carbon atoms designated as (a) and (b) in the Scheme 2.0. The formation of conjugated double bond was ascertained from δ values at 5.68, 5.92, 6.44 and 5.72 ppm. These shifts were assigned to carbon atoms named as (c), (d), (e) and (f) respectively in the Scheme 2.0. An indicative of 9Z and 11E isomer were assigned.

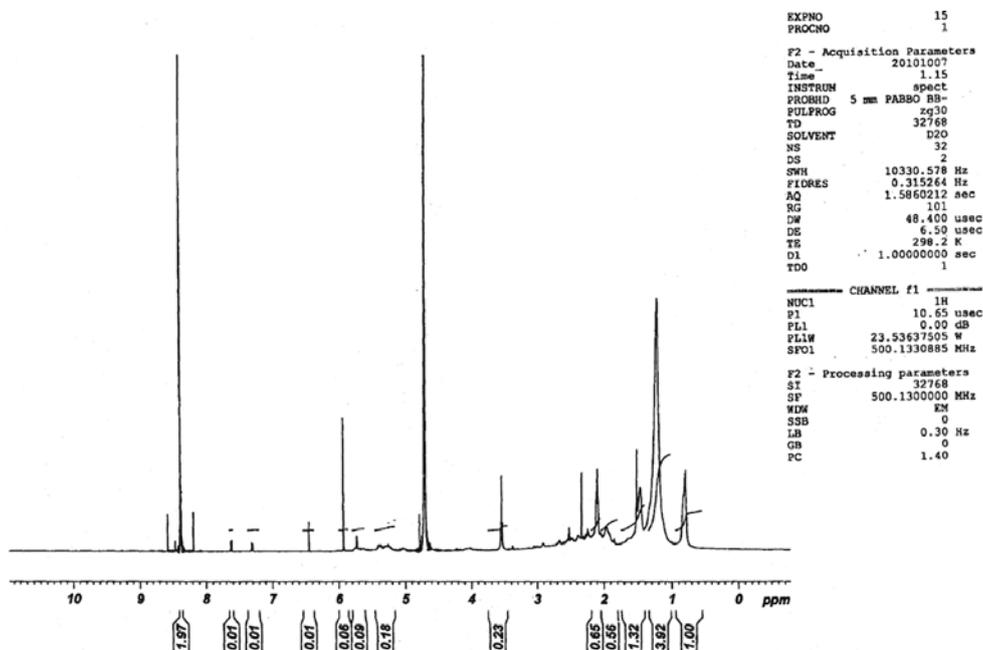


Fig. 3. ^1H NMR of MS.

The multiplet occurring at 3.57 to 3.56 ppm in the Figs. 4 (a) and 4 (b) was due to malenized carbon attached to the fatty acid chain and designated as x, y and z in Scheme 2.0. After the reaction with butanediol, the multiplet disappeared due to the formation of ester. Similarly δ values at 2.1 and 2.09 ppm were to $-(\text{CH}-\text{COOH})$ after malenization. The chemical shift at 1.42 ppm was from methylene

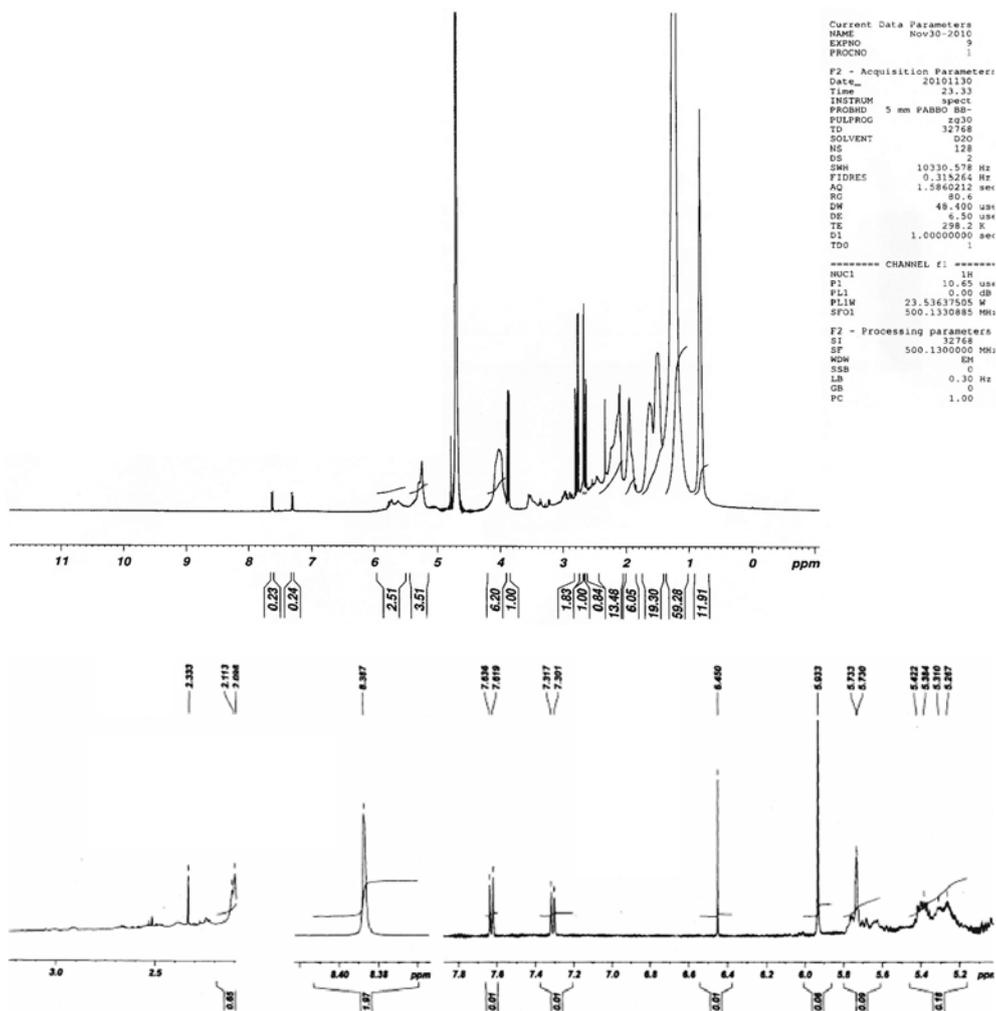


Fig. 4 (a) and (b). ¹H NMR of SDMS.

carbon atoms of butanediol. The ester formation with butanediol resulted in shifting of δ value from 3.6 to 2.7 ppm. These were from C1 and C4 carbon atoms of butanediol due to delocalization of ester groups.

LCMS Characterisation :

As a supportive characterisation, LCMS spectrum of SDMS (Fig. 5) was used for

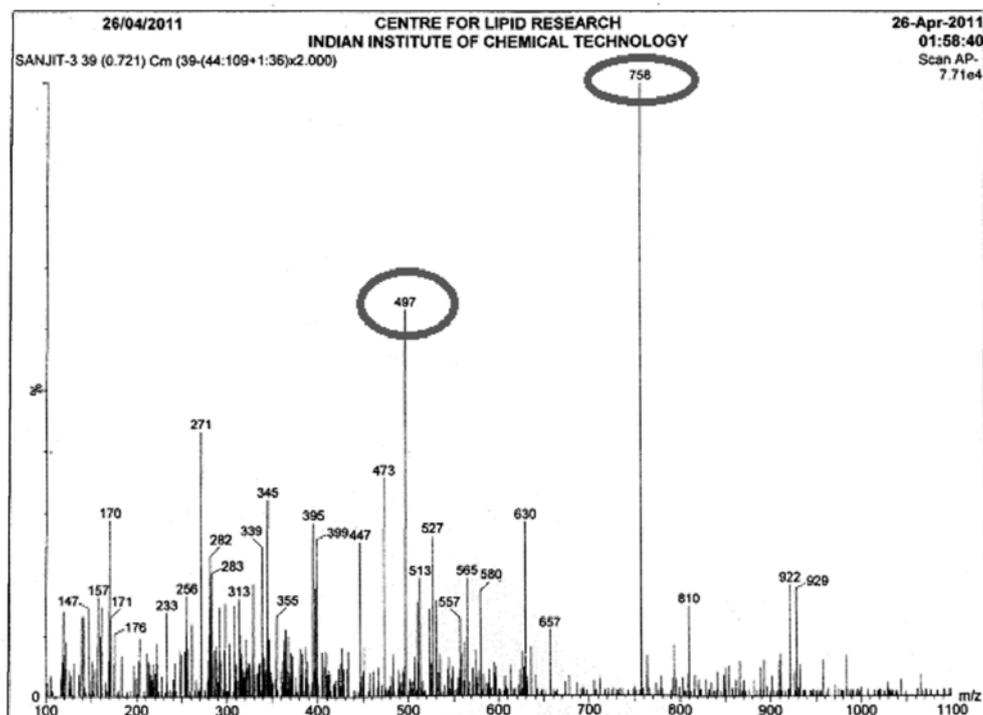


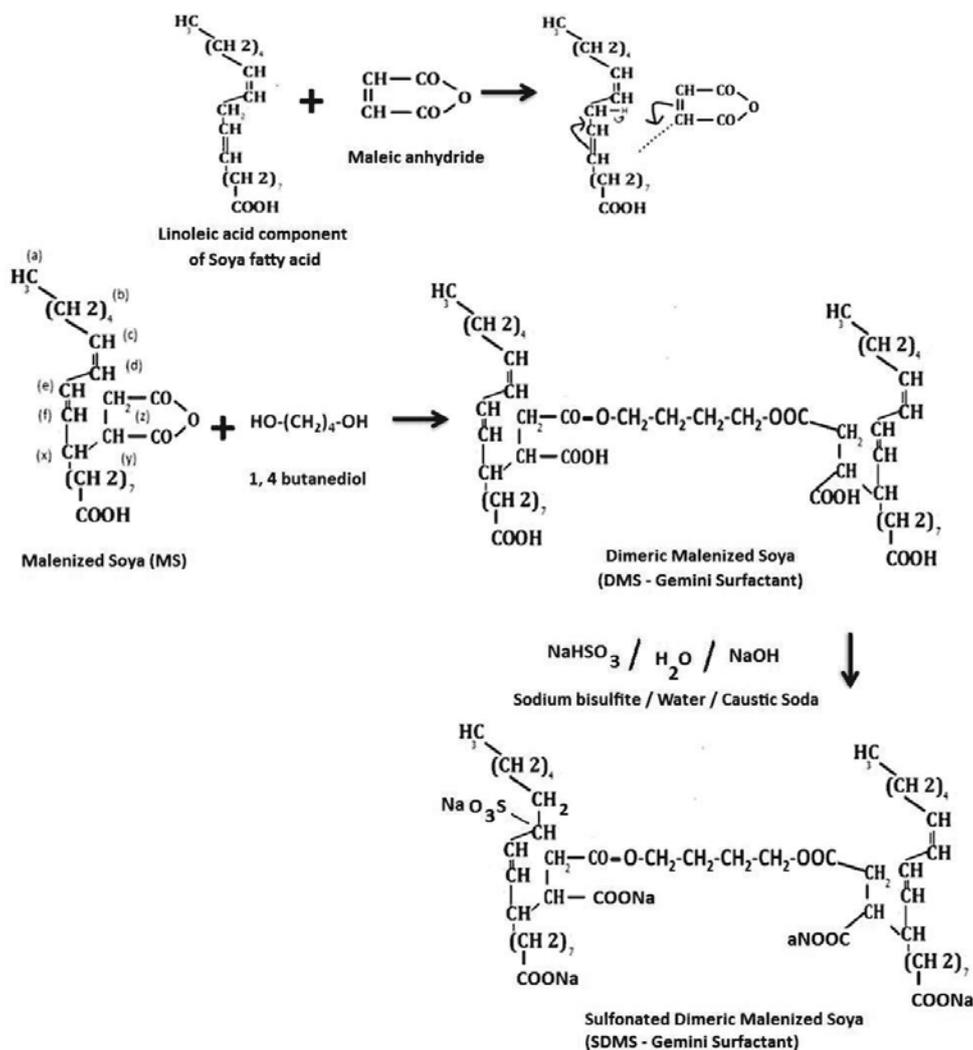
Fig. 5. LCMS of SDMS.

the identification of molecular weights of the fragmented components [35]. Fig. 5 showed different peaks, each corresponds to different types of fragments obtained from the targeted compound SDMS. They resulted not only from SDMS but also from the other byproducts and unreacted components.

The molecular structure of SDMS was given in Scheme 2.0. The molecular formula and the calculated molecular weight were $C_{48}H_{73}O_{15}Na_5S$ and 1036 respectively. For confirming the structure, we have evaluated two major abundant peaks i.e, 758 and 497 from Fig. 5.

Fragmentation happened between carbon atoms designated as m and n (Fig. 6) – mentioned as F1. As a result, a major fragment [36] obtained as M^+Na^+ . The molecular weight of the same calculated as 758 and confirmed through the peak at 758.

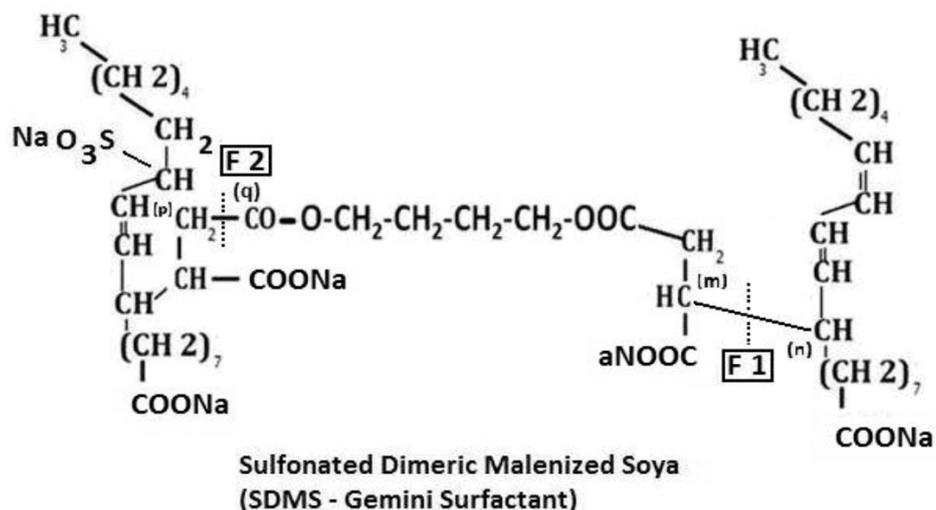
An another fragmentation was seen between carbon atoms designated as p and



Scheme 2.0 : Synthesis of the gemini surfactant SDMS.

q (Fig. 6) – mentioned as F2. This resulted in the peak at 497, which was exactly matched with the calculated molecular weight of the fragment.

The above data supported the formation of the compound and its structure.



F 1 - Fragmentation 1 - Molecular weight of parent compound - 1036
Molecular weight of fragment compound as M + Na⁺ - 758

F 2 - Fragmentation 2 - Molecular weight of parent compound - 1036
Molecular weight of fragment compound as M - 497

Fig. 6. Fragmentation pattern of SDMS in LCMS

SURFACTANT PROPERTIES

Malenised soya and Dimeric malenised soya were measured for the surfactant properties like surface tension at different concentrations, critical micelle concentration, foam stability and contact angle. (Table 1).

From Table 1, it was observed that at all the concentrations, surface tension was less in the case of dimeric product. At very low concentrations, the difference was found to be more and at high concentrations, the difference got slightly lowered. The ability to adsorb at the air-water interface was higher in the dimeric product. The tighter packing of the hydrophobic groups of the dimeric surfactant at the interface resulted in a more cohesive and stable interfacial film [2].

In the present study, critical micelle concentration of the dimer was almost 10 folds lesser than its monomer. The increase of hydrophobicity of the dimer resulted the lowering of CMC. The spacer reduced the intermolecular repulsion between head

TABLE 1.

Determination of surface active properties

Parameters	MS	DMS
Surface tension in mN/m		
Concentrations (% W/W) in water		
0.001	52.5	46.0
0.002	47.7	43.6
0.004	46.6	41.0
0.02	37.2	33.4
0.05	30.1	29.7
0.1	25.8	25.5
Critical micelle concentration (mol/L)	0.00529	0.000984
Foam stability		
(Foam at 5 th min./foam at 0 min × 100)	49.9	56.3
	Low stable	Meta stable
Contact angle for water in deg.	0	0

groups. Hydrophobic forces opposed by electrostatic repulsion among the ionic head groups at the micelle surface, drive the micellization [4]. Micelles are known to be disorganised assemblies with interior consisting of mobile hydrocarbon chains.

The micellization behaviour of gemini surfactant is qualitatively different from that of conventional surfactants. The lower CMC can be attributed to the increase in the number of hydrocarbon groups in the molecule. The CMC of gemini surfactant is a non-monotonous function of the number of spacer hydrocarbon groups.

Table 1 showed that the foam stability was better in the case of dimeric surfactant. Foam stability depends on the availability of hydrophobic groups and the spacer. The foaming ability was dependent on their structure. Again tighter packing of hydrophobic groups helped for greater foam stability.

As far as the contact angles concerned, both the surfactants showed similar trend.

Gemini surfactants are generally superior over conventional surfactant in terms of surface activity. This is due to the distortion of hydrophobic groups. In gemini

surfactant, two hydrophobic groups in a single molecule are more disruptive than individual chains in conventional surfactants. This in turn promotes the migration of a micelle to the air/water interface. Moreover, gemini surfactants can be used in small quantities as compared to conventional surfactants [37].

CONCLUSIONS

Anionic gemini surfactants have wide applications because of their high surface activity and low critical micelle concentration. They can be used as emulsifiers, dispersants, hydrotropic agents and also act as mild surfactants. Efforts have been made in the present work to design and develop a new class of gemini surfactants with improved surface active properties. As a part of the continuous research in this field, a new compound through esterification of malenised soya fat using 1,4-butanediol was attempted and a dimer was synthesized. The compound was sulfonated and chemically converted as sulfonated surfactant. The compound was characterized by FT-IR, ¹H NMR and LCMS techniques. The surfactant activity was analysed using the measurement of surface properties. The synthesized product can be tried in industrial applications. It will be a challenge for the research scientists to develop more cost effective and environmental friendly gemini surfactants for effective applications. The application of the synthesized surfactant was tested on the leather as a fatliquor and the results were published [38].

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REFERENCES

1. R. Janardhanan, Gunjan, V. Vijayabhaskar, M. S. L. Karuna, Y. Anjaneyulu and B. S. R. Reddy, A study of evaluation of sulphosuccinated polyethylene glycol ester based fatliquor, on different leather substrates, *Leather Age*, 10, 64 (2007).
2. S. K. Hait and S. P. Moulik, Gemini surfactants : A distinct class of self-assembling molecules, *Current Science*, 82, 9, 1101-1111 (2002).
3. M. J. Rosen, Geminis : A New Generation of Surfactants, *CHEMTECH*, 23, 30-33 (1993).

4. Dipti Shukla and V. K. Tyagi, Anionic Gemini Surfactants : A Distinct Class of Surfactants, *55*, 5, 215–226 (2006).
5. J. B. Niederl and A. E. Lanzilotti, *J. Am. Chem. Soc.*, *66*, 844–852 (1944).
6. C. A. Bunton, L. Robinson, J. Schaak and M. F. Stern, *J. Org. Chem.*, *36*, 2346–2350 (1971).
7. F. Devinsky, L. Masarova and I. Lacko, *J. Colloid Interface Sci.*, *105*, 235–239 (1985).
8. Y. P. Zhu, A. Masuyama and M. Okhara, Preparation and Surface Active Properties of Amphipathic Compounds with Two Sulfate Groups and Two Lipophilic Alkyl Chains, *J. Am. Oil Chem. Soc.*, *67*, 459–463 (1990).
9. Tai Shuxin, Gao Zhinong, Liu Xueguo and Zhang Qi, Synthesis and properties of novel alkyl sulphate gemini surfactants, *European Journal of Lipid Science and Technology*, Ahead of Print.
10. Sakai Kenichi, Umemoto Naoki, Matsuda Wataru, Takamatsu Yuichiro, Matsumoto Mutsuyoshi, Sakai Hideki and Abe Masahiko, Oleic acid based gemini surfactants with carboxylic acid headgroups, *Journal of Oleo Science*, *60* (8), 411–417 (2011).
11. Tian Zhiming, Deng Qigang and Sun Hong, Preparation, properties, and application of the gemini surfactants, *Huagong Shikan*, *22* (1), 61–63 (2008).
12. Fu Ji-feng, Yang Jian-xin and Xu Bao-chai, Preparation and properties of the gemini surfactants, *Jingxi Huagong*, *18* (1), 14–17 (2001).
13. Van Zon Arie, Bouman, Jan T, Deuling Henk H, Karaborni Sami, Karthaeuser Joachim, Mensen H. T. G Alfred, Van Ost Nico M and Raney Kirk H, The synthesis and performance of anionic gemini surfactants, *Tenside; Surfactants, Detergents*, *36* (2), 84–86 (1999).
14. Sakai Kenichi, Sakai Hideki and Abe Masahiko, Recent advances in gemini surfactants : oleic Acid-based gemini surfactants and polymerisable gemini surfactants, *Journal of Oleo Science*, *60* (4), 159–163 (2011).
15. Zhong Sheng, Gong Lijing and Zhang Linlin, Synthesis and Properties of a New Piperazine-Based Bicaudate Gemini Surfactant, *Journal of Dispersion Science and Technology*, *33*(7), 960–964 (2012).
16. F. M. Menger and C. A. Littau, Gemini Surfactants : A New Class of Self-Assembling Molecules, *J. Am. Oil Chem. Soc.*, *115*, 10083–10090 (1993).
17. Y. P. Zhu, A. Masuyama and M. Okahara, Preparation and Surface Active Properties of New Amphipathic Compounds with Two Phosphate Groups and Two Long-Chain Alkyl Groups, *J. Am. Oil Chem. Soc.*, *68*, 268–271 (1991).
18. Y. P. Zhu, A. Masuyama, Y. Kirito and M. Okahara, Preparation and Properties of Double- or Triple Chain Surfactants with Two Sulfonate Groups Derived From Acyldiethanolamines, *J. Am. Oil Chem. Soc.*, *68*, 539–543, (1991).

19. Y. P. Zhu, A. Masuyama, Y. Kirito, M. Okahara and M. J. Rosen, Preparation and Properties of Glycerol-Based Double-or Triple Chain Surfactants with Two Hydrophilic Ionic Groups, *J. Am. Oil Chem. Soc.*, 69, 626–632 (1992).
20. Jeffrey J. Scheibel, Connor Daniel and Fu Yi-Chang, Gemini polyhydroxy fatty acid amides, *United States Patent*, 5, 534, 197 (1996).
21. Briggs Catherine and Pit Alan, Non-ionic surface active compounds and photographic materials containing them, *United States Patent*, 4, 892, 806 (1990).
22. Marumo Hideo, Detergent composition, *United States Patent*, 3, 888, 797 (1975).
23. Marumo Hideo, A New detergent composition, *United States Patent*, 3, 855, 156 (1974)
24. Shan Yuhua and Wu Guoying, Synthesis and properties of sulphosuccinate mono (ethoxylated cottonseed oil alkylamide) ester disodium salt, *Jingxi Huagong*, 15(1), 6–9, (1998).
25. Tang Jun, Li Yujie, Han Xiaoping and Wang Qiang, Synthesis and properties of sodium 1, 4 butanediol bi sulfosuccinate diester, *Yingyong Huagong*, 35(3), 203, (2006).
26. Methods of sampling and test for oils and fats, IS : 548 : 1964, Part I.
27. Kremers F. J., The sulfonation of castor oil with sulfur trioxide. *J. Amer. Oil Chem. Soc.*, 48, 7, 314–317 (1971).
28. D. Rana, G. Neale and V. Hornof, Surface tension of mixed surfactant systems : ligno sulphonate and sodium dodecyl sulphate, *J. Colloid. Polym. Sci.*, 280, 775–778 (2002).
29. M. S. L. Kaurna, J. R. C Reddy B. V. S. K. Rao and R. B. N. Prasad, Lipase-mediated synthesis of alkyl ricinoleates and 12-hydroxy stearates and evaluation of the surfactant properties of their sulfated sodium salts, *J. Surfact. Deter.*, 8, 3, 271–276, (2005).
30. R.L. Bendure, Dynamic adhesion tension measurement, *J. Colloid .Int. Sci.*, 42 (1), 137–144 (1973).
31. P. Craun Gary, G. Hahn Kenneth and P. Rosekelly George, Styrenated maleinized fatty acid glyceride copolymer for aqueous dispersed binders in solvent free ambient dry paints, *Unites States Patent*, 6, 646, 085 (2003).
32. www.personal.une.edu.ac/ [4+2] Cycloaddition reaction
33. Socrates, *IR handbook*, (1982).
34. W.W.Simons, Ed., Sadtler research laboratories, The sadtler guide to NMR spectra (1983).
35. [http://en.wikipedia.org/wiki/Mass Spectrometry](http://en.wikipedia.org/wiki/Mass_Spectrometry).

36. James J. Pitt, Principles and Applications of Liquid Chromatography-Mass Spectrometry in Clinical Biochemistry, *Clin. Biochem Rev.*, 30 (1), 19–34 (2009).
37. B. S. Sekhon, Gemini (dimeric) Surfactants, The Two-Faced Molecules, *Resonance*, 9 (3), 42–49 (2004).
38. R. Janardhanan, V. Vijayabaskar and B. S. R. Reddy, Performance of Sulfonated Dimeric Malenised Soya Fatty Acid on Leather as a Fatliquor, *The Journal of the American Leather Chemists Association*, 107 (4), 128–136 (2012).