CHAPTER 3

SULFONATED MALENISED

SOYA FATTY ACID – A

GEMINI SURFACTANT
3.0 Introduction

Surfactants show interesting interfacial and bulk properties. These have a wide variety of uses which are mostly met by conventional surfactants. The conventional surfactant molecules are composed of a long hydrophobic hydrocarbon tail with an ionic or polar hydrophilic head, whereas a gemini surfactant has in sequence of a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail. The two terminal hydrocarbon tails can be either short or long. The two polar head groups can be either cationic or anionic or zwitterionic or non-ionic. The spacer can be either short or long, flexible or rigid. It need not be symmetrically disposed about the centre of the spacer. They are new type of classical surfactants and capable of forming self assemblies having two amphiphiles in a molecule chemically bonded through a spacer group as shown in Figure 3.1.

![Schematic representation of a gemini surfactant](image)

**Figure 3.1** Schematic representation of a gemini surfactant\(^{119}\)
The surface active efficiency of gemini surfactants are comparatively better than the conventional surfactants and have good water solubility. Their ability to form micelles and lowering surface tension characteristics are good as compared to normal conventional surfactants. They have good wetting, foaming, lime soap dispersing and hydrotropic properties along with good biodegrability.

Leather is a unique flexible sheet of material somewhat analogous to textiles, strong, durable, supple, soft, warm and porous. It is mainly a fibrous protein known as collagen and is composed of one continuous network of fibers. The various layers of the leather are as follows:

1. The thin outermost layer termed as epidermis.
2. The grain layer.
3. The juncture between the grain layer and the corium.
4. The major portion of the pelt known as the corium.
5. The flesh layer or the structure adjacent to the body tissues.

There are about 25 operations in the process of converting hides and skins into leather. One of the important step is fatliquoring and anionic fatliquors are the preferred choice because of their emulsifying properties, stability towards alkali, solubility, hydrotroping properties, low orders of toxicity, relatively low orders of irritation and also provides water white products\textsuperscript{120}. Gemini surfactants play an important role in deciding the performance of the fatliquoring agents.
3.1 Literature survey

Literature reports suggest that the subject is of interest due to the inherent properties of surfactants that could find applications from simple cleaning operations to sophisticated industrial applications. A number of gemini surfactants were reported in the literature. Also, gemini surfactants were disclosed by U.S. Patents. Relatively quite new and very few species have been reported in the prior art. A method for the preparation of a nonionic gemini surfactant was reported wherein the hydrophilic head was a sugar or carbohydrate moiety while the hydrophobic head was a long chain alkyl group and the two being joined by a short alkyl chain. Also, a number of nonionic gemini surfactant species in which the hydrophobic portion was comprised of a long chain lower alkyl or alkene while the hydrophilic portion was comprised of an ethoxylate group were reported.

Sugar based hydrophilic heads were also reported. Other surfactant structures were recently reported. In each case, a secondary hydroxyl group was sulfated, carboxylated or phosphated. Sulphosuccinate monoethoxylated cotton seed oil alkylamide ester disodium salt was reported. 1-Octadecanol was used as a material. Gemini surfactants used in the oil field were also reported from China.
The objective of this present research is to develop new, more effective, efficient surfactants and to apply on leather as a fatliquor. Therefore, efforts had been made to design and develop a new class of gemini compounds. There are no reports on the synthesis of a gemini surfactant having two hydrophilic and two hydrophobic groups, using esterification route as the bridge formation to the best of our knowledge.

### 3.2 Scope

A gemini surfactant having two hydrophilic and two hydrophobic groups using malenisation of soya fatty acid as a base was synthesized. Soya fatty acid was enriched in linoleic and oleic acids. The base was dimerised using 1,4-butanediol as a spacer. The prepared malenised surfactant was sulfonated using sodium bisulfite as a sulphonating agent.

The intermediates were characterised spectroscopically by IR, Proton NMR and LCMS. The surfactant properties such as surface tension at different concentrations, critical micelle concentration, foam stability, contact angle, emulsification power and zeta potential were measured. The new surfactant was substituted with reduced dosage in place of a conventional surfactant in a fatliquor formulation. Chemical parameters of the fatliquors were analysed and tested on leather.
The properties imparted by the fatliquor to leather were studied qualititatively and quantitatively. SEM studies of the treated leathers were carried out to study the morphology and penetration of fatliquor. The surface energy was calculated for the fatliquors. Particle size of the surfactant used in the test fatliquors correlated to the performance.

3.3 Experimental

3.3.1 Materials used for the synthesis and its application

Soya fatty acid of the following specifications was used for the study. 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 2% of other fatty acids. It was procured from M/s Versatile Chemicals Limited, Mumbai, India.

Other chemicals like maleic anhydride, para toluene sulphonic acid, 1,4-butane diol, sodium bisulfite and isopropyl alcohol were used as LR grade without any further purification. The reagents were procured from M/s Marlecha’s Scientific & Chemicals Pvt. Limited, Chennai, India. Vegetable oil of M/s South India Krishna Oil and Fats (Pvt.) Limited, Krishnapattinam, Andhra Pradesh, India, Mineral oil of M/s Indian Oil Corporation, Chennai, India, Chloroparaffin sulfonates of M/s Balmer Lawrie & Co. Limited, Chennai, India and Neutralization agent of M/s KLJ Resources Limited, Mumbai, India were of industrial grade products.
3.3.2 Methods of the synthesis

3.3.2.1 Synthesis of malenised soya (MS)

93.3g of soya fatty acid was heated for 1h at 150ºC under nitrogen, followed by the addition of 49g of maleic anhydride and 1.4g of para toluene sulphonic acid. The temperature of the oil bath was heated to 205 ± 5 º C and maintained at that temperature for 5h. The drop in the acid value of the soya fatty acid was checked to make sure that the reaction was completed.

3.3.2.2 Synthesis of dimerisation of malenised soya (DMS):

Malenized soya fatty acid was cooled from 150ºC to 120ºC and added 1.6g of para toluene sulphonic acid. 15g of 1,4-butane diol was added slowly in 5 portions, of 3g each. The esterification reaction was carried out at 120ºC for 3h. The drop in the acid value of the malenised soya fatty acid was checked to make sure that the reaction was completed. 36ml of xylene was added in a Dean & Stark apparatus. Water formed during the reaction was removed by refluxion in the Dean & Stark apparatus.

3.3.2.3 Synthesis of Sulfited dimeric maleised soya (SDMS):

The dimeric ester was cooled from 120ºC to 90ºC and 57.5g of sodium bisulfite dissolved in 77.5g of water and 15g of isopropyl alcohol were added. The reaction was continued at 90ºC for 3h. % Water content, pH and %SO₃ were analysed.
3.4 Reaction Mechanism

Linoleic acid component of soya fatty acid, which is non-conjugated and unsaturated, reacted with maleic anhydride at 200-210°C and malenised linoleic acid was obtained. Chemical reaction occurred 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 resulted in the movement of the double bond of the fatty acid chain to a conjugated double bond system, while the double bond carbon of maleic anhydride 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 so as to form the resultant structure. The –ene synthesis followed a pericyclic 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 200-210°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 π + 2 π 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 synthesis, which is a cycloaddition of 2s + 2π + 2π orbitals involving HOMO (Highest Occupied Molecular Orbital) and the allylic part of linoleic acid with LUMO (Lowest Unoccupied Molecular Orbital) of maleic anhydride to form the product. The Scheme 3.1 illustrates a similar -ene reaction of ethylene with propylene.

Scheme 3.1 Reaction mechanism of –ene reaction of ethylene with propylene type similar to the –ene synthesis of SDMS

Here, lower temperatures were used initially followed by quickly heating to higher temperatures. The prepared monomer having two molecules was chemically linked by a spacer which leads to changes in the physical and chemical properties.
3.5 Analytical methods used for the characterization of materials

Materials used were analysed for different specifications. Analytical methods were discussed in Chapter 2.0 and Chapter 3.0.

3.5.1 Saponification value

It is the number of milligrams of potassium hydroxide required to neutralize the fatty acid resulting from the complete hydrolysis of 1 gram of the sample.

A known weight of the sample was taken in a round bottom flask and added 25 ml of standard 0.5 N alcoholic potassium hydroxide (KOH) solution. It was added with porcelean bits to avoid bumping, during refluxing. The sample was saponified for 1 hour. After the saponification, the condenser was rinsed with methanol, cooled and titrated against standard 0.5 N hydrochloric acid (HCl) using phenolphthalein as an indicator. The end point was the disappearance of pink colour. The same reaction was carried out without the sample, for blank determination.

\[
\text{Saponification value} = \frac{(B-S) \times N \times 56.11}{W}
\]

Where

- **B:** Consumption of HCl for the blank,
- **S:** Consumption of HCl for the sample,
- **N:** Strength of HCl and
- **W:** Weight of the sample taken.
3.5.2 Iodine value

A known weight of the sample was taken into a clean dried iodine flask and added 20 ml of carbon tetrachloride (CCl₄). 20 ml of iodine monochloride solution was added and allowed to stand in the dark for 30 minutes. A blank test was also carried out simultaneously under similar experimental conditions. After 30 minutes, 15 ml of 20% potassium iodide solution (KI) and 50ml of water were added. This was titrated with standard 0.1N sodium thiosulphate (Thio). 1ml of starch was added and the titration was continued until the blue colour disappeared.

Iodine value = \frac{(B-S) \times \text{Normality} \times 12.69}{\text{Weight of the sample}}

Where 
- B: Thio solution required for the blank and
- S: Thio solution required for the sample

3.5.3 Freezing point

The material was heated till it got melted. It was cooled slowly till the material solidified. The temperature at which the melted mass got solidified was reported as the freezing point.

3.5.4 Gas chromatography-Mass Spectra (GCMS)

% Fatty acid distribution was analysed using Gas Chromatograph – Mass Spectra (GC-MS), Shimadzu GC 2010 make (GC-FID). DB 23 column of length 60m, ID 0.25 mm and film thickness 0.25 µm and the column temperature of 130-230° C were used.
3.5.5 % Sulphonate (SO₃) Content

3.5.5.1 Methylene blue indicator solution: 30 grams of sodium sulphate was added to 6.6 ml of concentrated sulphuric acid and 0.03 grams of methylene blue powder. It was made upto 1000 ml using distilled water.

3.5.5.2 Hyamine (Benzethonium chloride ) solution: 1.788 grams of hyamine was dissolved and made upto 1000 ml with distilled water.

3.5.5.3 Hyamine factor estimation: 10 ml of 0.5% sodium lauryl sulphate was added to 25 ml of chloroform and 25 ml of methylene blue indicator solution. It was shaken well and found that the methylene blue colour was in the bottom layer. The prepared hyamine solution was added gradually with a stirring till the upper layer (water) and the lower layer (chloroform) had the same intensity of blue colouration. The titre value was noted.

Factor for hyamine solution = \( \frac{27.4}{\text{Titre value}} \)

[\% SO₃ of sodium lauryl sulphate is 27.4 (99 % basis)]
3.5.5.4 Experimental method: 0.5 % solution of the sample was prepared and 10 ml was taken. It was added with 25 ml of chloroform and 25 ml of methylene blue indicator solution. It was shaken well and found that the methylene blue colour was in the bottom layer. The standardised hyamine solution was added gradually with a stirring till the upper layer (water) and the lower layer (chloroform) had the same intensity of blue colouration. The titre value was noted.

\[
\% \text{SO}_3 = \text{Titre value} \times \text{Factor of hyamine solution}
\]

3.6 Analytical characterization of the synthesis

The intermediates and the synthesized surfactants were analysed for the characterization.

During the first stage of the synthesis, acid value was found to be 305 during the first hour. Acid values after 3 and 5 hours were found to be 272 and 270 respectively.

During the second stage, acid values at the end of 1, 2 and 3 hours were found to be 157, 146 and 144 respectively.

Sulphonation was carried out in the third stage. The final sample was found to contain 61.0 % water, pH of 7.4 and %SO₃ on 100% basis was 2.6.
3.7 Reactions and structure of surfactant

The chemical reactions and the structure of the surfactant were shown in Scheme 3.2.

Scheme 3.2 – Synthesis of Gemini Surfactant
3.8 FTIR Characterisation

The IR spectra of SDMS (Figure 3.2) was interpreted for wave number and functional groups (Table 3.1).

Figure 3.2 – IR spectra of Gemini Surfactant (SDMS)
Table 3.1 – IR data of Gemini Surfactant (SDMS)

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Functional groups of SDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>3436</td>
<td>OH stretching of carboxyl groups with H bonding</td>
</tr>
<tr>
<td>2925</td>
<td>Asymmetric C-CH stretch of CH(_3)</td>
</tr>
<tr>
<td>2853</td>
<td>Symmetric C-H stretch of CH(_3)</td>
</tr>
<tr>
<td>1736</td>
<td>-C=O stretch of carbonyl or ester</td>
</tr>
<tr>
<td>1574</td>
<td>-C=C- conjugation</td>
</tr>
<tr>
<td>1197</td>
<td>Asymmetric stretching of ester</td>
</tr>
<tr>
<td>1045</td>
<td>Symmetric stretching of ester/ -SO3 symmetric stretching</td>
</tr>
<tr>
<td>976</td>
<td>-C=CH- deformation , aliphatic unsaturation</td>
</tr>
</tbody>
</table>

From the IR data, it was observed that the presence of carboxyl groups with H- bonding and carbonyl frequencies of the ester at 3436 cm\(^{-1}\) and 1736 cm\(^{-1}\) respectively. The asymmetric stretching of the ester was indicated at 1197 cm\(^{-1}\). Assymetric C-CH and symmetric C-H stretches of CH\(_3\) of Soya fatty acid were observed at 2925 and 2853 cm\(^{-1}\) respectively. Malenization resulted in the formation of conjugation by the migration of double bond in the fatty acid chain and was confirmed by the frequencies at 1574 cm\(^{-1}\) for conjugated –C=C- stretch and 976 cm\(^{-1}\) for –C=CH- deformation for aliphatic unsaturation. The formation of ester linkage and sulphonic salts in the final compound were confirmed unambiguously from the IR data.
3.9 $^1$H NMR Charaterisation

The $^1$H NMR spectra of MS and SDMS were shown in Figure 3.3 and 3.4.

Figure 3.3 – $^1$H NMR spectra of Malenised Soya (MS)
Figure 3.4 – $^1$H NMR spectra of Gemini Surfactant (SDMS)
In the Figure 3.3, the triplet protons of methyl group were assigned for the carbon atoms designated as (a) and (b) at 0.8 ppm and 1.5 ppm corresponding to the methylene protons of fatty acid (see Figure 3.5 for marking the atoms or the groups for discussion). The malenization reaction resulted in a conjugated structure in the fatty acid chain, while the maleic double bond carbon attached to the former non-conjugated double bond carbon of fatty acid. The formation of conjugated double bond was confirmed from $\partial$ values of hydrogen atoms attached to the carbon atoms at (c): 5.68, (d): 5.92, (e): 6.44 and (f): 5.72 ppm. An indicative of 9Z and 11E isomers were assigned.

![Figure 3.5 – Structure of Malenised soya (MS)](image-url)
The \(^1\)H NMR spectra of SDMS, gemini surfactant due to esterification with butanediol was given in Figure 3.4. The multiplets occurring around 3.57 to 3.56 ppm were due to malenized carbons attached to the fatty acid chain, designated hydrogen atoms attached to the carbon atoms (see Figure 3.5) as x, y and z carbon atoms. After reacting with butanediol, the multiplet disappeared due to the formation of ester. Similarly \(\partial\) values at 2.1 and 2.09 ppm were appeared corresponding to the \(-(\text{CH-COOH})\) after malenization. In gemini surfactant, the chemical shift value at 1.42 ppm was assigned for methylene carbon atoms of butanediol. The ester formation with diol resulted in shifting of \(\partial\) values from 3.6 to 2.7 ppm for C1 and C4 carbon atoms of butane-diol due to delocalization of ester groups.

### 3.10 LCMS Characterisation

Molecular weight was calculated using Liquid Chromatography-Mass Spectra (LC-MS), waters micromass quattro micro API model by mode APCI negative and direct infusion method.

The LCMS spectrum of SDMS was shown in Figure 3.6 and used for the identification of molecular weights of the fragmented components.
Liquid Chromatography-Mass Spectra (LCMS) is an important technique for determining the molecular mass of the compound. This method separates compounds chromatographically before they are introduced into the ion source and mass spectrometer. Mobile phase was a mixture of water and organic solvent. Mass spectrum provides molecular ion peaks corresponding to the molecular mass of the fragments.

Figure 3.6 – LCMS of Gemini Surfactant (SDMS)
The prepared sulfited gemini surfactant (SDMS) was subjected to LCMS, for the identification of the molecular weights of the components present in the surfactant through fragmentation. The possible expected structure was elucidated by the identification of molecular weights. A sample from a synthesis will probably contain other components chemically related to the targeted component. Occasionally, other components may form adducts with the analyte molecules as well. Being the natural sourced raw material, soya fatty acid, as expected had a quite number of components, which on further chemical modification, was reflected in the spectrum. Inspite of these technical difficulties in the analysis, major product was clearly confirmed by LCMS.

The molecular structure of SDMS was given in Scheme 3.2. The molecular formula and the calculated molecular weight were $\text{C}_{48}\text{H}_{73}\text{O}_{15}\text{Na}_5\text{S}$ and 1036 respectively. For confirming the structure, we have evaluated two major abundant peaks i.e, 758 and 497 from Figure 3.6.

Fragmentation happened between carbon atoms designated as $m$ and $n$ (Scheme 3.3) – mentioned as F1. As a result, a major fragment obtained as $\text{M}^+\text{Na}^+$. 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 q (Scheme 3.3) – mentioned as F2. This resulted in the peak at 497, which was exactly matched with the calculated molecular weight of the fragment.

The formation of the compound and its structure confirmed unambiguously from MS data.
3.11 Surfactant Properties

The prepared surfactants, MS and DMS were measured for the surfactant properties like surface tension, critical micelle concentration, foam stability, contact angle, emulsification power and zeta potential.

**Table 3.2: Determination of surface active properties**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>MS</th>
<th>DMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension (mN/M) of concentrations (% W/W) in water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>52.5</td>
<td>46.0</td>
</tr>
<tr>
<td>0.002</td>
<td>47.7</td>
<td>43.6</td>
</tr>
<tr>
<td>0.004</td>
<td>46.6</td>
<td>41.0</td>
</tr>
<tr>
<td>0.02</td>
<td>37.2</td>
<td>33.4</td>
</tr>
<tr>
<td>0.05</td>
<td>30.1</td>
<td>29.7</td>
</tr>
<tr>
<td>0.1</td>
<td>25.8</td>
<td>25.5</td>
</tr>
<tr>
<td>Critical micelle concentration (mol/L)</td>
<td>0.00529</td>
<td>0.000984</td>
</tr>
<tr>
<td>Foam stability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Foam after 5 minutes/Foam after 0 minutes) X 100</td>
<td>49.9</td>
<td>56.3</td>
</tr>
<tr>
<td>Contact angle for water in deg.</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Emulsification power of 1% solution (sec)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time taken for 10 ml aqu. separation</td>
<td>9.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Time taken for 20 ml aqu. separation</td>
<td>16.0</td>
<td>38.0</td>
</tr>
<tr>
<td>Zeta Potential (mv)</td>
<td>-38.4</td>
<td>-62.2</td>
</tr>
</tbody>
</table>
The methods were discussed in Chapter 2.0 and Chapter 3.0. The results were given in Table 3.2.

### 3.11.1 Foam stability

Foam stability\textsuperscript{155,156} was determined using Ross-Miles pour foam apparatus. Surface tension at different concentrations of the samples in distilled water of MS and DMS were shown in Figures 3.7 and 3.8.

![Surface tension at different concentrations of MS](image-url)

**Figure 3.7 – Surface tension at different concentrations of MS**
Figure 3.8 – Surface tension at different concentrations of gemini surfactant (SDMS)

Zeta potential curves of MS and DMS were shown in Figures 3.9 and 3.10.
Figure 3.9—Zeta potential curve of MS
Figure 3.10 – Zeta potential curve of gemini surfactant (SDMS)
3.12 Behaviour of surfactant properties

3.12.1 Surface tension

Surface tension is the property of the surface of a liquid that allows it to resist an external force. This property is caused by cohesion of like molecules and is responsible for the behaviour of the surfactant. In the present study, we have measured surface tension of the dimeric surfactant (DMS) and its conventional analogue MS. We have found that at all the concentrations, surface tension was lowered in the case of dimeric product. At very low concentrations, the difference was found to be more and when we move to high concentrations, the difference got slightly lowered. But, in all the cases, surface tension of DMS was low when compared to MS. The ability to adsorb at the air-water interface was higher in dimeric product. The tighter packing of the hydrophobic groups of the dimeric surfactant when compared to its monomer at the interface results in a more cohesive and stable interfacial film. Similar results were reported earlier.

3.12.2 Critical Micelle Concentration

Critical micelle concentration is the concentration above which micelles form and almost all additional surfactant added to the system goes into micelles. This value of CMC was the parameter that provides the capability of the surfactants forming assemblies.
Hydrophobic forces opposed by electrostatic repulsion among the ionic head groups at the micelle surface, drive the micellization. In the present study, CMC of the dimer was almost decreased by 10 folds compared to its analogue. This may be assumed due to the increase of hydrophobicity. Packing of the hydrophobic groups in dimer at the air-water interface was small and hydrophilic group was closer than that found in its analogue. The lower CMC can be attributed to the increase in the number of hydrocarbon groups in the molecule. The butanediol spacer reduces the intermolecular repulsion between head groups.

3.12.3 Foam stability and contact angle measurements

A foam is a property of a substance that is formed by trapping many gaseous bubbles in a liquid or solid. Anionic dimeric surfactants show good foaming properties. Foam stability was better than its conventional analogue. Foam stability of MS and DMS on comparison shows good improvement. The stability of the dimer was fairly improved. Foam stability depends on availability of more number of hydrophobic groups and the spacer.

The contact angles in both the surfactants showed similar trend.
3.12.4 Emulsification power

Emulsification provides the surfactant ability and gives the emulsification capacity. The emulsification capacity was comparatively higher because of the presence of more hydrophilic groups in the gemini surfactant. In the present study, it was found that the emulsification power of gemini surfactant shows two fold increase in capacity than the conventional surfactant. Gemini surfactant emulsifies the free oil available in the fatliquor to the maximum possible extent providing deeper penetration and better absorption. In the conventional surfactant system, neutral oil available in the system would deposit on the surface of the leather due to lesser emulsification power. It was observed that the oil deposited on the fibrils of the leather in the case of gemini surfactant due to higher emulsification power.

The tighter packing of the hydrophobic groups of the gemini surfactant compared to the conventional surfactant at the interface results in a more cohesive and stable interfacial film which indicates the higher emulsification power. Strong interaction in the system at interfaces or in mixed micelles occurs because of more ionicity than the conventional surfactants. Packing of the hydrophobic groups in the gemini surfactant at the aqueous solution – air interface was closer than that found in the conventional surfactants.
Higher emulsification capacity of the gemini surfactant than the conventional surfactant was also due to the distortion of water by hydrophobic groups. In the case of gemini surfactant, two hydrophobic groups in a single molecule were found to be more disruptive than individual chains in conventional surfactants. This in turn promotes the migration of a micelle to the air/water interface.

In the gemini surfactant, certain spacers can form hydrogen bonds with water and thereby, reduce the unfavourable hydrocarbon-water contacts, making it easier for spacers to locate at the micelle-water interface. Furthermore, additional hydration at the level of the spacer chain should mitigate the coulombic repulsion between the head groups. All these factors all act together to help gemini surfactant molecules to aggregate at a lower concentration.

The surfactants with the higher emulsification property, besides having the property of being able to emulsify and disperse free fats and oils, possess better capacity of binding to leather collagen through electrostatic and hydrophobic interactions.
3.12.5 Zeta potential

Zeta potential applies to the electrical charges existing in liquid emulsions. Zeta potential is a measure of charges carried by particles suspended in a liquid, measuring in millivolts. The difference in electrical charge between the dense layer of ions surrounding the particle and the bulk of the suspended fluid. The stability of the surfactant dependent upon the degree of ion absorption\textsuperscript{160}, and therefore, on the zeta potential. 

The magnitude indicates the potential stability of the surfactant. The higher value of zeta potential represents higher stability of the system. From the values, it was inferred that the conventional sulfonated surfactant was having moderate stability, compared to the gemini surfactant which was found to have very good stability.

In the case of gemini surfactant, zeta potential was higher due to the increase of surface charge density\textsuperscript{161} of the micelles. More zeta potential lowers critical micelle concentration and thereby makes easier aggregation of micelles. The stability of the formulations might be based on the steric effect arising from the adsorbed surfactants on the leather surface.
The hydrophobic part of the surfactant was assumed to be anchored\textsuperscript{162} on the stable phase surface, whereas the hydrophilic part was assumed to be directed outwards into the continuous phase of water.

One approach known to stabilize an emulsion was to confer an electrostatic charge to the droplet surface which will result in droplet repulsion and less droplet coalescence\textsuperscript{163}.

Colloidal particles dispersed in a solution were electrically charged due to their ionic characteristics and dipole attributes. This charge, which can be negative resulting in anionic emulsions or positive producing cationic emulsions\textsuperscript{164} was known in the art as the zeta potential.
3.13 Application of the gemini surfactant as fatliquors

Fatliquors were prepared by blending a mixture of vegetable oil (25%), mineral oil (5%), chloroparaffin sulfonate (15%), neutralizing agent (3%) and sulfonated surfactant (12%). The composition was adjusted to 100% using water.

The conventional sulfonated surfactant used in the original fatliquor and the same was replaced by the synthesized gemini surfactant sulphonated dimeric malenised soya fatty acid (SDMS) in the test fatliquors, without further purification by keeping all the other ingredients and conditions identical.

(i) In the original fatliquor (FL R), the sulfonated surfactant was kept at 12%.

(ii) The sulfonated dimeric surfactant was substituted by 8% in the first fatliquor (FL 1) and 4% in the second product (FL 2).

Prepared fatliquors FL R, FL 1 and FL 2 were analysed for chemical parameters. Colour in loviobond gardener scale found to be 12 with clear clarity. % Water was 40.0 and pH was 8.0. Emulsions were prepared from the fatliquors using hard water upto 2000 ppm of calcium chloride and found to be stable.

Wet blue cow leathers were treated with the prepared fatliquors using FL 1 Vs FL R and FL 2 Vs FL R, using the general leather fatliquoring process, described in Chapter 2.0
3.14 Performance evaluation

3.14.1 Properties of leathers

Wet blue cow leathers treated with the prepared fatliquors FL 1 against FL R, and FL 2 against FL R were evaluated qualitatively and quantitatively. Detailed results were given in Tables 3.3 and 3.4.

**Scale of grading**

1. Very poor
2. Poor
3. Good
4. Very good
5. Excellent

**Table 3.3 – Organoleptic properties of FL 1 Vs FLR and FL 2 Vs FLR**

<table>
<thead>
<tr>
<th>Properties</th>
<th>FL 1</th>
<th>FL R</th>
<th>FL 2</th>
<th>FL R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feel</td>
<td>4.8</td>
<td>4.7</td>
<td>4.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Inner softness</td>
<td>4.8</td>
<td>4.7</td>
<td>4.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Grain touch</td>
<td>4.8</td>
<td>4.8</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Stretch</td>
<td>4.8</td>
<td>4.7</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Bleaching</td>
<td>4.7</td>
<td>4.7</td>
<td>4.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>

**Table 3.4 – Physical testing results of FL 1 Vs FLR and FL 2 Vs FLR**

<table>
<thead>
<tr>
<th>Testings</th>
<th>FL 1</th>
<th>FL R</th>
<th>FL 2</th>
<th>FL R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (Kg/Cm2)</td>
<td>108.2</td>
<td>105.9</td>
<td>145.3</td>
<td>114.8</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>68</td>
<td>67</td>
<td>82</td>
<td>73</td>
</tr>
<tr>
<td>Grain crack strength (Kg)</td>
<td>68</td>
<td>33</td>
<td>76</td>
<td>73</td>
</tr>
<tr>
<td>Distention 1</td>
<td>12.9</td>
<td>11</td>
<td>12.3</td>
<td>12.2</td>
</tr>
<tr>
<td>Bursting strength (Kg)</td>
<td>78</td>
<td>75</td>
<td>87</td>
<td>85</td>
</tr>
<tr>
<td>Distention 2</td>
<td>13</td>
<td>12.9</td>
<td>12.8</td>
<td>12.8</td>
</tr>
</tbody>
</table>
The leather performance factors of the fatliquors FL 1 and FL R were compared. We could observe that the feel, inner softness, stretch and bleaching were found to be very close on the scale of qualitative assessment, whereas grain touch was almost the same. The tensile and bursting strengths were much closer whereas, grain crack strength was better.

It was observed that the grain touch was equal when compared with the fatliquors FL 2 and FL R, whereas the other properties like feel, inner softness, stretch and bleaching were better. The tensile strength was found to be better compared to grain crack strength and bursting strength which were closer. From all the results, FL 2 was a better fatiquor where the leather performance properties were enhanced even with 66% dosage reduction using the newly prepared gemini surfactant.

Treated leather samples were enclosed in the end of the thesis.

### 3.14.2 Scanning electron microscopic (SEM) analysis

SEM studies of grain pattern of leathers fatliquored with FL 2 and FL R were given in Figures 3.11 and 3.12, at a magnification of X 1000.
Figure 3.11 – Scanning electron micrographic photograph [x 1000 magnification] of grain surface of the leather fatliquored using FL 2, containing sulfonated dimeric malenised soya fatty acid surfactant.
Figure 3.12 – Scanning electron micrographic photograph [x 1000 magnification] of grain surface of the leather fatliquored using FL R, containing conventional sulfonated surfactant

Fiber splitting up of the grain in both the leathers were very well observed. In the case of the gemini surfactant FL 2, the penetration was still better than the other one which was established by the qualitative and quantitative assessment of leather parameters.
Leather parameters\textsuperscript{165} were derived from the fibril bundles to distort and slip when the stress was applied. To get better fiber bundle splitting, the structure should not stick to each other by the adhesions created during drying and the lubricant should be able to allow the fibers to slide over one another\textsuperscript{166}. These parameters were achieved by the addition of fatliquors. The effectiveness of fatliquoring depends on the degree of the penetration of the fatliquor which was predominated by the surfactant present in the system. In our study, both the conventional and the experimental fatliquors were containing sulfonated surfactants. But penetration of the neutral oil into the fibrils of the leather was better in the case of gemini surfactant because of its higher surface activity.

Addition of gemini surfactant to the lubricating oil decreases effectively the interfacial tension between oil and water in order to penetrate lubricating emulsion, which resulted in deeper penetration showing higher performance. Also, the gemini surfactants destabilize collagen fibers and impairs the mechanical properties to leather due to of the presence of higher hydrophilicity. This property provides better solubility to form a stable solution.
The gemini surfactants besides having the property of being able to emulsify and disperse fats and oils, possess the capacity of binding to proteins through electrostatic and hydrophobic interactions. It was also to be noted that the quality of the grain surface of the treated leather depends to a great extent on the size of the hair follicles. If leather processing reduces the hair follicle mouth to a small almost closed aperture, the grain surface will have a higher natural gloss.

Phase behaviour of mixed systems involving oil, water and surfactants was an important area of research in the field of surfactant chemistry whose study often was found to be tedious and time consuming. In the leather application as fatliquors, surfactants were used in formulations containing mixtures of different compounds, and synergism can often be observed. Synergism was defined as the condition in which the properties of a mixture were better than those attainable with the individual components separately, where the aggregation of the surfactants play a crucial role. Conventional surfactants form spherical aggregates, whereas gemini surfactants forms either thread like or rod like micelles. When the fatliquor was applied before the leather was dried, it reached the fibrils and that on drying will remain within the cohesive domains and as a result, on drying all the adhesions in the leather became weaker.
### 3.14.3 Surface Energy of the Fatliquors

The interfacial surface tension of oil with water was very small and measuring contact angle of oil on wet leather was difficult to measure. This problem was handled by separating the oil phase and the emulsifier phase from the fatliquor and applying the Young’s equation (Figures 3.13 and 3.14).

The determination of contact angles over wet leather was not practicable due to the fact that the leather contains both hydrophilic and hydrophobic regions. These experiments were performed on two different surfaces such as extremely hydrophobic (Teflon) and extremely hydrophilic (Glass) surfaces.

![Young's model for oil phase of a fatliquor](image)

\[ \gamma_{SV} - \gamma_{SO} = \gamma_{OV} \cos \theta_C \]

**Figure 3.13 – Young’s model for oil phase of a fatliquor**

\( \gamma_{SV}, \gamma_{SO}, \) and \( \gamma_{OV} \) are the interfacial tensions between leather and vapour, leather and oil, oil and vapour respectively. The equilibrium contact angle that the drop makes with the surface is denoted by \( \theta_C \).
\[ \gamma_{SV} - \gamma_{SWe} = \gamma_{W e V} \cos \theta_c \]

**Figure 3.14 – Young’s model for aqu. emulsifier phase of a fatliquor**

\( \gamma_{SV} \), \( \gamma_{SWe} \), and \( \gamma_{W e V} \) are the interfacial tensions between leather and vapour, leather and aqu. emulsifier, aqu. emulsifier and vapour respectively. The equilibrium contact angle that the drop makes with the surface is denoted by \( \theta_c \).

The important characteristics of a liquid surfactant was its ability to freely spread over the surface of the object being experimented. Surface energy was quantified in terms of the forces acting on a unit length at the solid-air or the solid-liquid interface.

Wettability of a material was its tendency to make liquids spread out over its surface and was the direct function of surface energy\(^{170}\). Higher the surface energy of a material, the more the liquid will spread out over the surface.
Surface energy values of the fatliquors FLR and FL 2 were calculated after the separation of the oil and surfactant components. Results were given in Table 3.5. Wetting efficiencies of FLR and FL 2 were found to be closer, and this explains the equal performance of these two fatliquors.

### Table 3.5 – Surface energy values of fatliquors

<table>
<thead>
<tr>
<th>Component</th>
<th>Surface tension (mN/M)</th>
<th>Contact angle – glass (°)</th>
<th>Contact angle – Teflon (°)</th>
<th>Surface energy – glass (mN/M)</th>
<th>Surface energy – Teflon (mN/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil of FLR</td>
<td>20.93</td>
<td>4.3</td>
<td>29.3</td>
<td>20.9</td>
<td>18.3</td>
</tr>
<tr>
<td>Surfactant of FLR</td>
<td>23.7</td>
<td>7.7</td>
<td>24.2</td>
<td>23.5</td>
<td>21.6</td>
</tr>
<tr>
<td>Oil of FL2</td>
<td>23.66</td>
<td>3.5</td>
<td>35</td>
<td>23.6</td>
<td>19.4</td>
</tr>
<tr>
<td>Surfactant of FL 2</td>
<td>26.9</td>
<td>11.3</td>
<td>24.8</td>
<td>26.4</td>
<td>24.4</td>
</tr>
</tbody>
</table>

The adhesive forces\(^{171}\) between the fatliquor and the leather will compete against the cohesive forces of the fatliquor. Fatliquors with weak cohesive bonds and a strong adhesive forces with leather will tend to spread over the material. Fatliquors with strong cohesive bonds and weaker adhesive forces with leather will tend to form droplet when in contact with the leather. Fatliquor will fill the voids in the leather until an opposing force balances the capillary pressure.
Performance in terms of surface energy of a fatliquor based on gemini surfactant than a conventional surfactant was due the geometrical shape of the molecules. In the gemini surfactant, two molecules have been chemically linked by a spacer which leads to changes in the physical and chemical properties\textsuperscript{172}. One of the main effects of introducing the spacer was to impose an additional geometrical constraint on the packing of surfactant molecules and therefore, to influence their aggregate shape.

The dependence of the specific area of gemini surfactant at the air/water interface on the spacer was also important for the activity. In the present study, we have used short spacer which will lead to large packing parameter, may account for the formation of preferred micelles. Also, the hydrophobic repulsion leads to shorter end-to-end distances and therefore to smaller specific surface area.

The geometrical effect of the spacer, the interaction among the surfactant monomers and the conformational entropy of the spacer plays an important role on the surfactant activity.
### 3.14.4 Particle Size of SDMS used in making the test fatliquors

Particle size is a notion introduced for comparing dimensions of liquid particles as droplets. Size distribution analysis of gemini surfactant (SDMS) used in making fatliquor (FL 2) was given in Figure 3.15.

![Figure 3.15 Particle size distribution analysis of SDMS used in FL 2](image-url)
Mean size of gemini surfactant (SDMS) used in making the fatliquor (FL 2) was found to be 23.64 microns. The minimum and maximum sizes were found to be 11 and 87 microns respectively. This was comparatively having lower size species. When the fatliquor was prepared using SDMS and applied on leather, smaller the species will penetrate better and yields the required performance\textsuperscript{173}. From the count chart, it was understood that the spectrum was having narrow Gaussian which is required for effective performance.

Higher particle size will lead to creaming process which was determined by the droplet size, difference in the density and viscosity of the surrounding medium. The particle size of SDMS was small, leading to higher surface area resulting faster and deeper penetration into leather during fatliquoring. Smaller particles had dominant cohesive and adhesive forces compared to particle weight, whereas in bigger particles gravity plays a dominant role. Lesser particle size resulted in increased solubility and better performance. Smaller particles and narrower distributions produce better performance than larger particles and broad distributions.
3.15 Conclusions

Anionic gemini surfactants have wide applications because of their high surface activity and low critical micelle concentration values. They can be used as emulsifiers, dispersants, hydrotropic agents and also act as mild surfactants. Efforts have been made to develop a new class of compounds with improved surface active properties due to the need for new and efficient requirements. As a part of the continued research in the field to develop novel surfactants for value addition, a newer compound through esterification of malenised soya fat using 1,4-butanediol was attempted and a dimer was synthesised. The dimer was sulphonated and chemically converted as sulphonated surfactant. The intermediate compound and the surfactants were characterized by FT-IR, $^1$H NMR and LCMS techniques. The surfactant activity was analysed using the measurement of surface properties.

When the conventional surfactant in a fatliquor formulation was replaced by the new sulphonated gemini malenised soya fatty acid, bridged with butane diol. The performance on the wet blue cow leather matched with the control even with reduced dosage to the extent of 66%, which leads to enormous cost reduction and less environmental pollution.