CHAPTER 4

EFFECT OF SPECIFIC ADDITIVES ON THE DEGREE OF SULFONATION
4.0 Introduction

Surfactants are able to modify the interfacial properties of a system by changing the surface tension. It is the amphiphilic nature of surfactant molecules that makes them bifunctional. In recent years, accompanied by the progress of society and the development of science and technology towards eco-friendly chemicals, the application fields of surfactants have expanded. Sulfosuccinate type anionic surfactants are surface active metal salts of either monoester or diester of sulfosuccinic acid. These are obtained by reacting maleic acid anhydride with hydroxyl groups carrying molecules, followed by sulfonation of the intermediate product, an ester. These surfactants are of great interest because of their excellent properties such as foaming, strong wetting, emulsifying and solubilising properties, extraordinary surface activity, high effectiveness in reducing surface tension, biodegradability, great mildness and low critical micelle concentration.

Sulphosuccinate type anionic surfactants are the sodium salts of alkyl esters of sulphosuccinic acid resembling the alkyl sulphonates. These are of two types:

(a) Monoesters \([\text{NaSO}_3\text{-CH(COOR)-CH}_2\text{COOH}]\) commonly known as half ester. The monoesters are good foamers and mild to skin and eyes.
(b) Diesters \([\text{NaSO}_3\text{-CH(COOR)-CH}_2\text{COOR}]\); The diester is a poor foamer, quite irritating and has low solubility. In industries, diesters are used as wetting agents and dispersants.

Sulfosuccinates are having extensive applications in personal care products, household products, textiles, polymers, leather, printing and agriculture industries. Because of its nature, they have better usage as a surfactant in the manufacture of fatliquors which plays a crucial role on the physical properties of finished leather.

4.1 Literature study

Works on sulfosuccination of maleic monoester was reported by M/s American Cyanamid Co. Limited. A series of sulphosuccinic esters were prepared and used acid value as the process control during ester preparation\(^{177}\). Castor oil, jojoba oil, lard oil and other glycerides based sulfosuccinates\(^{178-184}\) were developed and reported. Sulfosuccinates based alkyl phenol ethoxylates\(^{185}\) and lanolin\(^{186}\) were also reported. The effect of presence of the moisture\(^{187}\) in the reactants during sulfosuccination process was investigated recently. Reaction optimistion of esterification and sulfonation of the manufacture of sulfosuccinates\(^{188-189}\) were also reported.
Chemistry of bisulfite addition to ethylenic double bonds was well documented\textsuperscript{190} in the literature. The bisulfite addition to mono- and di-alkyl esters of maleic acid was a common method to produce the corresponding sulfonate derivatives. However, the effect of addition of special additives like phase transfer catalyst, non-ionic wetting emulsifier and co-solvent on the degree of sulfosuccination have not been carried out systematically so far.

4.2 Scope

In the present research, the degree of sulfonation of maleic acid monoester as % sulfonate content, for the control batch analysed. The experiment was carried out in the presence of specific additives such as phase transfer catalyst, non-ionic wetting emulsifier and co-solvent individually. % Sulfonate contents were analysed for all the experiments. The prepared sulfosuccinates were analysed for emulsification power, zeta potential, surface tension and particle size. Reaction conditions for fixation of better degree of sulfonation were optimized.

Fatliquors prepared out of the control batch sulfosuccinate and maximum sulfonate content sulfosuccinate obtained in this research, were applied on wet blue full chrome cow leather. The properties of the resultant leathers studied along with the SEM studies. Effect of specific additives discussed and correlated with the performance on the leather.
4.3 Experimental

4.3.1 Materials used for the synthesis and its application

Lauryl maleate monoester (LAME) (Acid value: 160, pH: 6.0) of M/s Balmer Lawrie & Co. Limited, Chennai, India used for the study. Other chemicals like sodium bisulfite (SBS), tetrabutyl ammonium bromide (TBAB) and isopropyl alcohol (IPA) were used as LR grade without any further purification and procured from M/s Marlecha’s Scientific & Chemicals Pvt. Limited, Chennai, India. Lauryl alcohol 8 moles of ethoxylate (LA8EO) of M/s India Glycols Limited, Kashipur, Uttarakhand, 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.

4.3.2 Methods of the synthesis

4.3.2.1 Control batch\textsuperscript{191}

LAME (284g) was sulfonated using 120g sodium bisulfite dissolved in 480g water. Reactants were maintained at 70-75°C for 3h.
4.3.2.2 Experiment 1 (E1 - Addition 5% phase transfer catalyst)

LAME (284g) was sulfonated using 120g of sodium bisulfite dissolved in 480g of water and 45g tetrabutyl ammonium bromide. Reactants were maintained at 70-75°C for 3h.

4.3.2.3 Experiment 2 (E2 - Addition 5% non-ionic emulsifier)

LAME (284g) was sulfonated using 120g of sodium bisulfite dissolved in 480g of water and 45g lauryl alcohol 8 moles of ethoxylate. Reactants were maintained at 70-75°C for 3h.

4.3.2.4 Experiment 3 (E3 - Addition 5% co-solvent)

LAME (284g) was sulfonated using 120g of sodium bisulfite dissolved in 480g of water and 45g isopropyl alcohol. Reactants were maintained at 70-75°C for 3h.

Preparation details were given in Table 4.1

<table>
<thead>
<tr>
<th>Batch</th>
<th>LAME (g)</th>
<th>SBS (g)</th>
<th>Water (ml)</th>
<th>TBAB (ml)</th>
<th>LA8EO (ml)</th>
<th>IPA (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>284</td>
<td>120</td>
<td>480</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E1</td>
<td>284</td>
<td>120</td>
<td>480</td>
<td>45</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E2</td>
<td>284</td>
<td>120</td>
<td>480</td>
<td>-</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>E3</td>
<td>284</td>
<td>120</td>
<td>480</td>
<td>-</td>
<td>-</td>
<td>45</td>
</tr>
</tbody>
</table>
4.4 Surfactant properties

Surfactant properties such as %SO₃, surface tension and emulsification power of sulfosuccinates of E1, E2 and E3 along with the control batch were shown in Table 4.2. Zeta potential and particle sizes were shown in Table 4.3. The methods were discussed in Chapter 2.0 and Chapter 3.0.

Table 4.2 Surfactant properties sulfosuccinates

<table>
<thead>
<tr>
<th>Batch</th>
<th>% SO₃ (on 100% basis)</th>
<th>Surface tension (0.05% solution) (mN/M)</th>
<th>Emulsification power of 1% solution (Time in sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10ml</td>
</tr>
<tr>
<td>Control</td>
<td>5.2</td>
<td>32.92</td>
<td>40</td>
</tr>
<tr>
<td>E1</td>
<td>6.9</td>
<td>32.11</td>
<td>45</td>
</tr>
<tr>
<td>E2</td>
<td>11.3</td>
<td>29.05</td>
<td>70</td>
</tr>
<tr>
<td>E3</td>
<td>14.6</td>
<td>31.16</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 4.3 Zeta potential and particle size of sulfosuccinates

<table>
<thead>
<tr>
<th>Batch</th>
<th>% SO₃ (on 100% basis)</th>
<th>Zeta Potential (mv)</th>
<th>Particle Size (Microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Min</td>
</tr>
<tr>
<td>Control</td>
<td>5.2</td>
<td>-83.5</td>
<td>11</td>
</tr>
<tr>
<td>E1</td>
<td>6.9</td>
<td>-93.8</td>
<td>22</td>
</tr>
<tr>
<td>E2</td>
<td>11.3</td>
<td>-100.1</td>
<td>10</td>
</tr>
<tr>
<td>E3</td>
<td>14.6</td>
<td>-111.6</td>
<td>37</td>
</tr>
</tbody>
</table>

The data on particle size distributions of control, E1, E2 and E3 batch sulfosuccinates were given in the following Figures 4.1, 4.2, 4.3 and 4.4 respectively.
Figure 4.1 - Particle size distribution of control batch sulfosuccinate

Figure 4.2 - Particle size distribution of E1 batch sulfosuccinate
Figure 4.3 - Particle size distribution of E2 batch sulfosuccinate

Figure 4.4 - Particle size distribution of E3 batch sulfosuccinate
%SO₃, zeta potential, surface tension and particle size of the surfactants were given in Figures 4.5, 4.6, 4.7 and 4.8.

**Figure 4.5 - %SO₃ content of sulfosuccinates**

**Figure 4.6 - Zeta potential of sulfosuccinates**
Figure 4.7 - Surface tension of sulfosuccinates

Figure 4.8 - Particle size of sulfosuccinates
4.5 Sulfonate contents of the surfactants

The amount of sulfonate present in the sulfo succinate plays an important role in deciding the surface activity, which in turn is a crucial factor that decides the performance of the fatliquor on leather. Higher the sulfonate content, the reaction conversion was higher and the performance on leather was better by improving the leather properties such as softness, whiteness and surface touch. The major concern is about achieving maximum improvement in leather properties for industrial applications. Most of the results appear to clearly suggest that the conversion was indeed self-limiting. A postulate for the self-limiting nature of the process is that sulfo succination occurs via an interfacial process, whereby the ester has to migrate to the aqueous droplet interface. At the beginning of the sulfo succination, addition of sodium bisulfite with the double bond of the ester, thereby forms the initial surfactant. The same stabilizes the droplets and the process begins with a particular amount of water present, which is probably defined by the concentration of sodium bisulfite initially used. As the process progresses, a part of the ester continuously gets converted to the surfactant and these preferentially occupy the interfacial sites at the aqueous droplet interface. This in turn inhibits further migration of fresh ester to the interface and therefore limits the conversion.
It was felt that the limiting conversion could be able to overcome by the addition of phase transfer catalyst or non-ionic wetting agent or co-solvent. Accordingly, three separate experiments (E1, E2 and E3) were performed and obtained the higher sulfonate contents. Table 5.2 showed that % sulfonate content of the control batch was 5.2. The usage of phase transfer catalyst in sample E1 increases the sulfonate content by 1.33 folds. By employing non-ionic wetting agent in sample E2 increases the sulfonate content by 2.17 folds. Further, addition of co-solvent in sample E3 increases the sulfonate content by 2.8 times compared to the control experiment.

4.6 Effect of co-solvent

Sulfosuccination is basically the result of two phase reaction in which the sulfitation occurs only in the ester base. The slow rate of dissolution of the ester in the water medium produces lower sulfonate content. Addition of isopropyl alcohol (IPA) as a co-solvent in E3 converted the reaction as a single phase process. IPA dissolves both reactants into one phase so that the two reactants can be physically in contact with one other and provides an opportunity to chemically react. This increased the rate of reaction by making the ester soluble in the solvent by increasing the contact of the reactants192.
The formation of micelles takes place in the process due to the presence of IPA and reflected in terms of hydrophobic effect\textsuperscript{193-194}. Addition of IPA in E3 has been known to produce marked changes in the critical micelle concentration due to the tendency of IPA either to break or make the water structure through solvation\textsuperscript{195} of the hydrophobic tail of the initially formed surfactant. This acts as water structure breaker and decreases the hydrophobic effect resulting into an increase in the CMC of ionic surfactants.

Main driving force behind the formation of micelles is hydrophobic effect. The total hydrophobic effect is the combination from the surfactant and also from the co-solvent. Consequently, the local concentration of the co-solvent molecules around the surfactant monomers becomes larger than the average of the bulk.

The hydrocarbon of the co-solvent is getting associated with the molecules of the surfactant and thereby leading to delay the aggregation of the surfactant monomers to form micelles. This results in CMC changes.
The other factors such as hydrogen bonding ability of co-solvent\textsuperscript{196-202}, the changes in the polarity\textsuperscript{203} or hydrophobicity of IPA in E3 were also expected to play a crucial role in determining the micellar behaviour of the surfactants. The presence of IPA in water reduced the dielectric constant\textsuperscript{204} of the medium and thereby decreased the dissociation of the surfactant monomers and micelles as well. It was expected that the hydrophobic tail of the initially formed surfactant interacts with the hydrocarbon hydrophobic part of the organic solvent by the movement of the surfactant molecules from the interface to the bulk of the solution. This resulted in higher reaction rate and conversion, yielding the maximum sulfonate content as observed in Table 5.2.

4.7 Effect of emulsifier

Addition of non-ionic emulsifier, LA8EO in E2 physically surround one reactant and transport\textsuperscript{205} the first reactant to the second reactant. This allowed the two reactants to come into physical contact and thereby make them to react chemically.
LA8EO reduces the viscosity of the surrounding system by providing better control of the reaction to increase degree of sulfonation as observed in E2. In particular, homogeneity of the medium was also achieved which appears to be a prime requirement for better conversion. Both lipophilic and a hydrophilic poles are present in emulsifier. The lipophilic part bonds with the ester and the hydrophilic part bonds with the water facilitating the reaction at a faster rate.

Emulsifier stabilizes the reactants to form films at droplet’s surface and impart mechanical stability. It lowers the interfacial tension of the two phases. In the absence of emulsifier, the reaction system was a suspension (under stirring) with two separate phases and the reaction rate and the conversion were very slow as depicted in the case of control batch. Addition of LA8EO to E2 leads to micellar catalysis\textsuperscript{206}, where the lipophilic reactants were solubilised in the emulsifier micelles, and the swelled micelles disperse in water phase containing hydrophilic reactants. This will enable the reaction interface area between oil phase reactants and water phase reactants was enlarged greatly. The interface magnifying effect as well as electrostatic interaction and the concentrating effect results in dramatic increase in the reaction rates\textsuperscript{207-208}. 
Above CMC, the number of micelles increased with the addition of emulsifier resulting in fast reaction with a higher conversion. The increase in the addition of LA8EO induces micelles to expand, which in turn caused slow increase of oil/water interfacial area, resulting in gradually slowing down of the reaction without significant change in the conversion. The catalytic ability of the emulsifier could be attributed to its solubilization ability. In addition, the emulsifier can make reaction conditions gentle, effectively inhibit side reactions to occur and expected to enhance the efficiency of the reaction.

### 4.8 Effect of phase transfer catalyst

The addition of tetrabutylammonium bromide (TBAB) in E1 was found to be versatile synthetic technique applied to intensify the slow heterogeneous reactions of liquid-liquid or liquid-solid reactants. It decreases the reaction activation energy, accelerate reaction speed by making conditions convenient and inhibit side reactions. All these factors influence to increase the %SO$_3$ in sulfosuccinates.
The primary function of TBAB is to move an ion in a reactive state from one phase to a second phase. It is believed that it performs a true catalytic function by first disassociating from its anion, then associating with a different anion in the first phase and carrying the anion in a reactive state across the phase boundaries between the first and the second phases. After the ion reacts with a constituent in the second phase, TBAB reassociates with an anion and returns to the first phase in its original form to catalyze another phase transfer. TBAB promotes ion pair formation and simultaneously disturbs mass transfer across the interface.

In E1, the anion was transferred gradually from the aqueous phase into the organic phase by the intervention of an onium salt. In our research work, the sulfite was extracted in the form of onium salt into the organic phase and the onium sulfite then reacted with the ethyleneic double bond to form sulfosuccinate. The reaction conditions employed were rather mild, so that the possibility of side reactions, such as catalytic decomposition was considerably reduced.
For a phase transfer catalyst to be effective, it should deliver one reactant from its normal phase to the phase of another reactant such that the first reactant gets facilitated to react with the other reactant. Following the reaction between the two constituents, the phase transfer catalyst should be regenerated and then recycled to the first phase in order to catalyze the transfer of another reactant.

The quaternary ammonium salts have their unique capability to homogenise both aqueous and organic liquids. There were several advantages of being employed as a phase transfer catalytic systems in the industrial processes such as an increased reaction rate, mild reaction temperature and pressure, and avoiding the employment of expensive anhydrous or aprotic solvents.

4.9 Behaviour of surfactant properties

Surfactant properties like surface tension, emulsification power and zeta potential showed from Table 4.2 and 4.3 that the measurements were in accordance and direct agreement with the surfactant activity of the sulfosuccinates.
4.9.1 Surface tension

Surface tension was decreasing with the increase in the sulfonate content as expected. Surface tension of the control batch was 32.92 mN/m. As the surfactant activity increased, there was a reduction of surface tension. These values were decreased to 32.11 mN/m for E1 and 31.16 mN/m for E3. Similarly, in the case of emulsification power, the surfactant activity was only due to sulfonate content in the case of E1 and E3 whereas, there was an additional effect due to the added emulsifier. Hence, slightly further marginal reduction of surface tension of 29.05 mN/m was observed in E2.

4.9.2 Emulsification power

Emulsification power showed a positive variation with respect to the sulfonate content. Separation times for 10ml and 20ml for control batch were found to be 40 and 87 seconds respectively. The corresponding values increased to 45 and 100 for E1 batch fatliquor. There was a slight variation observed in the case of E2, where external emulsifier was added. The observed values were 70 and 147 seconds, whereas the same for E3 were 60 and 139 seconds respectively. Emulsification power was the capacity of the surfactant to bind the neutral oil present in any formulation. In the control, E1 and E3, emulsification power was only due to the sulfosuccinate component only.
In the case of E2, there was a combination of emulsification power of sulfosuccinate as well as the added external emulsifier. Hence, the value was slightly higher than that of E3, even though it had slightly lower sulfonate content than E3. Otherwise the values for the separation of 10ml and 20ml separation of neutral oil increases with the increase in the sulfonate content.

4.9.3 Zeta potential

In the case of zeta potential, there was an increased trend observed with the increase in the sulfonate content. Zeta potential values of the control batch, E1, E2 and E3 were found to be -83.5, -93.8, -100.1 and -111.6 mv respectively. Magnitude of zeta potential indicates the potential stability of the sulfosuccinate surfactant. As the sulfonate content increased, the potential stability increased and showed positive increase in zeta potential. Higher zeta potential provides better stability which appears to be an important factor in the fatliquor formulation.

4.9.4 Particle size

The particle size measurements from Table 4.3 showed that there were not much variation between the sulfosuccinates of different sulfonate contents. The observed values for control batch, E1, E2 and E3 were 19.8, 42.4, 39.8 and 59.1 microns respectively.
The relationship between particle size and the degree of sulphonation was not found to be linear\textsuperscript{217} as expected. Rather particle size was slightly increased with increase in sulfonate content. It showed slightly negative trend in E2, whereas positive trends were observed in E1 and E3. It appears that the sulfonate content had not played any role at all. The added additives like TBAB, LA8EO and IPA changed the particle size of the surfactants slightly.

### 4.10 Application of sulfosuccinated surfactants as fatliquors

Fatliquors were prepared as a formulation comprising of vegetable oil (12.5\%), mineral oil (10\%), chloroparaffin sulfonate (22.5\%) and sulfosuccinated surfactant (20\%). The composition was adjusted to 100 \% using water. The surfactants were control batch sulfosuccinate in FL-Control fatliquor and E3 batch sulfosuccinate in FL E3 fatliquor. The fatliquors were applied on full chrome wet blue cow leather of thickness 1.1 mm, against each other. The properties and scanning electron micrographs of the resultant leathers were studied.
4.11 Performance evaluation

4.11.1 Properties of leathers

Full chrome wet blue cow leathers treated with the prepared fatliquors FL Control against FL E3 were evaluated qualitatively and quantitatively. Properties of the resultant leathers such as softness, whiteness, surface touch, tensile strength and grain crack strength were shown in Table 4.4. Fatliquoring process and the methods of the assessment of leathers were discussed in Chapter 2.0.

Scale of grading

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FL Control</th>
<th>FL E3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softness</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Whiteness</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Surface touch</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Tensile strength (Kgs/Sqcm)</td>
<td>296</td>
<td>358</td>
</tr>
<tr>
<td>% Elongation</td>
<td>89</td>
<td>83</td>
</tr>
<tr>
<td>Grain crack strength (Kgs/cm)</td>
<td>344</td>
<td>380</td>
</tr>
<tr>
<td>Distention mm</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
The performance of fatliquors from the control batch and E3 batch were compared. E3 batch showed better performing fatliquor very clearly by improving the properties of softness, whiteness and surface touch, each to the extent of 11%. Tensile and grain crack strengths were improved by 21% and 11% respectively. The difference of degree of sulfonation of 2.17 times played the critical role in determining the improved performance.

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

Higher surfactant activity certainly imparted better leather performance parameters. The possible reason appears to be that a lower content of emulsifier in a fatliquor results in neutral oil depositing on the surface of the leather, resulting in lower performance. The other important criteria for the leather performance was the stability of the fatliquor emulsion which depends mainly on the sulfonate content of the surfactant. When the degree of sulfonation was low, it leads to an emulsion with poor stability, which would deposit oil on the surface of the leather. The stable emulsion deposits oil on the fibrils of the leather and able to penetrate better into the leather for good absorption.
The performance depends on the particle size also. When the particle size distribution was homogeneous as shown in Figure 5.4, the penetration into the leather was deeper. In our present study, the average count was uniformly distributed in the case of E3 compared to the control experiment.

Stability of the emulsifier gives the strength for the leather. Higher the SO₃ content, better will be the stability which in turn yield higher strength to the leather. The SO₃ content for the control and E3 were found to be 5.2% and 14.6% respectively and explains the difference. The effectiveness of fatliquoring depends on the degree of penetration of the fatliquor which was predominately dictated by the surfactant activity.

4.11.2 Scanning electron microscopic (SEM) analysis

Grain pattern of fatliquored leathers at a magnification of 300 x were shown in Figures 4.9 and 4.10.
Figure 4.9 - SEM photomicrograph of FL control at a magnification of x 300
The fibre splitting of the grain was very well observed in Figure 6.10. The fatliquoring composition having E3 surfactant facilitates better penetration into leather. This resulted in better lubrication of fibres and reflected in tremendous improvement in the performance of all properties.
4.12 Conclusions

During the sulfosuccination of the maleate monoester, addition of phase transfer catalyst, non-ionic wetting emulsifier and co-solvent found to improve the degree of sulfonation by 33%, 117% and 180% respectively. Sulfonate content has a direct effect on emulsification power, zeta potential and surface tension. The effect of additives such as phase transfer catalyst, non-ionic wetting agent and co-solvent play an important role in deciding the particle size. Judging from the conditions employed, this study has great prospects for industrial applications and patentability of this process.

When two fatliquors prepared using sulfosuccinate having 5.2% and 14.6% sulfonate content by employing different experimental conditions and applied on wet blue leather. The fatliquor prepared out of sulfosuccinate having 14.6% sulfonate content imparted better leather performance in all the aspects of softness, whiteness surface touch, tensile strength and grain crack strength.