CHAPTER 2

DIETHYLAMINO LAURYL ITACONATE – AN AMPHOTERIC SURFACTANT
2.0 INTRODUCTION

Surfactants\textsuperscript{56} are amphiphilic molecules that are capable of undergoing self-assembly into aggregated systems such as monolayers (eg., micelles) and bilayers (eg., vesicles). These unique molecules generally consist of a polar head group and one or two hydrophobic tail(s). As a consequence of the hydrophobic effect, the surfactants within the aggregated assemblies are oriented with their polar head groups exposed to the aqueous phase while their hydrophobic tails face away from the aqueous phase, thereby forming a hydrophobic core. Organized self-assembled surfactant phases have received a lot of attention recently possibly as viable reaction and templating media. However, conventional surfactant structures are of limited use due to their dynamic nature.

Amphoteric surfactants prepared through a novel route via the synthesis of polymerisable surfactants have received considerable attention because of their extensive industrial applications. They show high emulsion stability to salts responsible for the hardness of water, as well as to alkali salts. By virtue of the amphoteric character, the surfactants can be formulated along with cationic, anionic and also nonionic ingredients during its applications.
Fatliquoring is the last wet chemical process in the leather making process and is the application of mixture of oils and emulsifiers to leather. It is the process in which the leather fibers are lubricated so that after drying, they will be capable of slipping over one another\(^{57}\). It is an important process in the manufacture of leather which can give the leather a supple and plump handle, and improve its physical capabilities\(^{58}\). As a consequence, the leather acquires softness and a degree of water proofing\(^{59}\). It lubricates the fibres thereby preventing adhesion as well as glueing after drying, making the leather soft, pliable and flexible\(^{60}\).

It was shown that the amount of surfactant that must be applied to leather to achieve the desired properties of the product exceeds by ten fold the amount calculated to coat the collagen fibrils with a monomolecular layer, although these properties were retained when most but not all the applied material was extracted\(^{61}\). Current methods for lubricating leather, however, employ oils and surfactants that have been known to destabilize collagen fibers and to impair the mechanical properties of leather\(^{62}\). The important factors involved in the fatliquoring mechanisms\(^{63}\) are charge on the leather, emulsion stability, particle size distribution of an emulsion, ratio of emulsifier to neutral oil, viscosity and interfacial tension of oils. Softness depends on the ability of the oil to be emulsified and carried into the leather\(^{64}\).
2.1 Literature survey

Polymerizable surfactants (‘surfmers’)\textsuperscript{65}, have received much attention especially over the last 15 years. Surfmers offer potential for developing hybrid nanosized reaction and templating media due to their constrained geometries. A wide variety of surfmers have been synthesized and studied by different groups worldwide\textsuperscript{66-71}. A vast amount of literature exists in this field and there are a number of excellent reviews\textsuperscript{72-76}. Surfmers have been developed for enhancing kinetic and/or mechanical stability of molecular assemblies in aqueous solutions\textsuperscript{77}. This means that polymerized structures are not sensitive to dilution effects and that polymerized assemblies persists even below the critical micelle concentration of the original non-polymerised micelles. The factors that are important for effective performance are the reactivity of the polymerizable unit, its location and the solubility of the surfmer in aqueous medium, which in turn is governed by its critical micelle concentration\textsuperscript{78}.

Itaconic acid has been extensively studied with regard to its polymerization kinetics, role of bulky substituents, chain stiffness and glass-transition temperatures\textsuperscript{79-85}. Being a polymerisable dicarboxylic acid, it has the potential of being readily derivatized to generate polymerisable surfactants.
The conjugate addition of nucleophiles to electron-deficient alkenes is an important reaction and has wide applications in organic synthesis\textsuperscript{86}. The addition of amines to \(\alpha,\beta\)-unsaturated carbonyl compounds particularly produce the \(\beta\)-amino derivatives which are useful intermediates in the synthesis of a large number of products with a wide range of biological activity\textsuperscript{87}. Synthesis of a number of amphoteric surfactants through various methods and its application as a fatliquor were reported in the literature\textsuperscript{88-99}.

The physical characteristics of the leather such as break, extensibility and tensile strength, as well as the comfort properties of the leather, depend on fatliquoring. However, there are no reports on the conjugate Michael addition of an amine to a polymerizable surfactant having \(\alpha,\beta\)-unsaturated carbonyl group to yield an amphoteric surfactant and the development of fatliquor for leather processing to the best of our knowledge.

2.2 Scope

A new amphoteric compound “diethylamino-lauryl itaconate” (DEALI), through the conjugate Michael addition of an amino group, “diethylamine” to a polymerisable anionic surfactant, “lauryl itaconate” (LI) surfmer having \(\alpha,\beta\)-unsaturated carbonyl group, was synthesized by the esterfication of lauryl alcohol and itaconic acid.
LI and DEALI were characterized spectroscopically using IR and proton NMR spectroscopy. CMC, contact angles (Glass and Teflon), surface energy (Glass and Teflon), emulsification power, zeta potential, particle size properties of LI and DEALI were measured. The isoelectric point of DEALI was determined. The surface tension of LI and DEALI at different concentrations were also measured. Fatliquors were separately prepared using DEALI and LI. The properties imparted to leather by the surfactants were evaluated.

2.3 EXPERIMENTAL

2.3.1 Materials used for the synthesis and its application

Lauryl alcohol, itaconic acid, para toluene sulphonic acid, sodium hydroxide and diethylamine were used as LR grade reagents 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.
2.3.2. Methods of the synthesis

2.3.2.1 Synthesis of polymerisable anionic surfactant, lauryl itaconate (LI)

1 mole (186g) of lauryl alcohol was heated at 105°C for 15 min. to remove moisture present, followed by the addition of 1 mole of (130g) of itaconic acid and 1% of para toluene sulphonic acid (3.2g). The temperature of the oil bath was raised to 115 ± 5 °C and maintained the temperature for 4h. The drop in the acid value was checked to make sure that the reaction was completed. After the completion of the esterification, pH was adjusted using sodium hydroxide.

The experimental set up was given in Figure 2.1

![Figure 2.1 – Experimental setup of the synthesis](image)
2.3.2.2 **Synthesis of amphoteric surfactant, diethylamino-lauryl itaconate (DEALI)** 1 mole (298g) of LI was added slowly over a period of 30 min. at room temperature to 1 mole (73g) of diethylamine. Reactants were stirred at 30-32°C as a neat mixture for 5h\(^{100}\). After the reaction, pH was adjusted using formic acid.

2.3.3 **Reactions, mechanism and structures of the surfactants**

The chemical reactions, mechanism and the structures of LI and DEALI were shown in Scheme 2.1.

2.4 **Analytical characterisation of surfactants**

Acid value during the second hour was found to be 220. After 3 and 4 hours, the same were 169.7 and 166 respectively. After neutralization, pH was found to be 8.0. After the completion of the reaction, % water and pH were analysed as 18.0 and 12.5 respectively. Final pH was found to be 7.0.

2.4.1 **Analytical methods for the characterisation**

2.4.1.1 **Acid value\(^{101}\)**

It is the measure of the free fatty acid content of the sample. It is the number of milligrams of potassium hydroxide required to neutralize 1 gram of the sample.
Scheme 2.1 – Synthesis of LI and DEALI

\[ \text{Lauryl alcohol} + \text{Itaconic acid} \xrightarrow{\text{PTSA, 110 - 120°C, 4 h}} \text{Lauryl itaconate (LI)} \]

\[ \text{Lauryl itaconate (LI)} + \text{Diethylamine} \xrightarrow{\text{30 - 32°C, Neat, 5 h}} \text{Diethylamino Lauryl itaconate (DEALI)} \]
A known weight of the sample was dissolved in a pre-neutralised solvent [methanol:benzene : 1:1 V/V]. The mixture was titrated against standard 0.1 N alcoholic potassium hydroxide after the addition of phenolphthalein indicator. The end point was the appearance of the pink colour. Acid value was calculated using the following equation.

\[
\text{Acid value} = \frac{V \times N \times 56.11}{W}
\]

Where \(V\) = Volume of alcoholic KOH consumed,
\(N\) = Strength of alcoholic KOH and
\(W\) = Weight of the sample taken.

### 2.4.1.2 % Water content

A known weight of the sample was taken in a 1000 ml boiling flask containing approx. 25 ml of xylene which was attached to the water condenser through graduated Dean and Stark set up. The contents were heated to a boiling point where the available water in the sample was collected in the receiver till clear solution obtained. The sides of the condenser were washed with xylene. The amount of water collected was noted

\[
\% \text{ Water content} = \frac{\text{Amount of water collected} \times 100}{\text{Weight of the sample taken}}
\]
2.4.1.3 pH

10 grams of the sample was taken and diluted to 100 grams using demineralised water. pH was measured through precalibrated Labindia make pH meter.

2.5 FTIR characterisation

FTIR spectrum was taken using KBr pellet on BRUKER, IFS, 66V FT-IR.

The IR spectra of LI and DEALI were shown in Figures 2.2 and 2.3.

Figure 2.2 – IR spectrum of LI
Figure 2.3 – IR spectrum of DEALI
The characteristic peaks representing the functional groups were given in Table 2.1. Common functional groups in both surfactants were compared from literature\(^{103}\) and had same vibrational frequencies as mentioned in the Table 2.1.

**Table 2.1 – IR data of LI and DEALI**

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Functional group</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>2955</td>
<td>Assymetric C-CH stretch of CH(_3)</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>2852</td>
<td>Symmetric C-H stretch of CH(_3)</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>1737</td>
<td>-C=O stretch of carbonyl ester</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>1466</td>
<td>-CH2-CO stretching</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>1241</td>
<td>-C-O-C asymmetric stretching</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>1180</td>
<td>Assymetric stretching of ester</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>721</td>
<td>Consecutive CH(_2) groups</td>
<td>LI and DEALI</td>
</tr>
<tr>
<td>947</td>
<td>-CH out-of-plane deformation of aliphatic unsaturation of type CH(_2)=CHOCOR</td>
<td>Only in LI</td>
</tr>
<tr>
<td>866</td>
<td>-CH(_2) out-of-plane deformation of aliphatic unsaturation of type CH(_2)=CHOCOR</td>
<td>Only in LI</td>
</tr>
<tr>
<td>1351</td>
<td>C</td>
<td>Only in DEALI</td>
</tr>
<tr>
<td></td>
<td>-C-N-C deformation</td>
<td>Only in DEALI</td>
</tr>
<tr>
<td>771</td>
<td>-C-N-C deformation</td>
<td>Only in DEALI</td>
</tr>
</tbody>
</table>
Characteristic peaks observed for LI at 947 and 866 cm\(^{-1}\) were due to the presence of aliphatic unsaturation of the type CH\(_2\)=CHOCOR. When LI was reacted with diethylamine, the group was attached as a Michael type conjugate addition of nucleophile to electron-deficient alkene. As a result, the compound was converted as a saturated surfactant. Hence, peaks at 947 and 866 cm\(^{-1}\) were not present in the spectra of DEALI, confirming the formation. In the spectra of DEALI, peaks were present at 1351 and 771 cm\(^{-1}\) due to the deformation of –C-N-C functional group. This absorption appeared only after the reaction of LI with diethylamine and was absent in the spectra of LI.

The formation of ester in LI and the addition of amine to α,β-unsaturated carbonyl compound of LI resulted in the formation of amphoteric functional group in DEALI were confirmed unambiguously by IR spectroscopy.

2.6 \(^1\)H NMR spectroscopic characterisation

\(^1\)H NMR spectrum was taken using CDCl\(_3\) as a solvent for esters and d\(_3\) - acetone as a solvent for surfactant bases, on JEOL GSX 400, NB FT NMR.

The \(^1\)H NMR spectrum of LI and DEALI were shown in Figures 2.4 and 2.5.
Figure 2.4 – $^1$H NMR spectra of LI
Figure 2.5 – $^1$H NMR spectra of DEALI
The common functional groups present in LI and DEALI were found to have the same chemical shifts as observed in the figures. The shifts at 0.9 and 1.28 ppm were due to the presence of SP³ hybridized protons (C-H’s) of saturated carbon atoms of lauryl (CH₃ type) group of the surfactants. The chemical shift at 4.1 ppm was due to the presence of ester group of type –(OCOR). This shift occurred due to oxygenated SP³ hybridized protons (C-H’s) of ester functional group.

The characteristic chemical shift of LI at 4.8 ppm was due the presence of protons of aliphatic unsaturation of the type (-CH₂=CH-). During the conversion to amphoteric surfactant, the double bond got saturated by the addition of a nucleophile. Hence, the shift at 4.8 ppm disappeared in DEALI.

The chemical shifts corresponding to DEALI were present around 2.3–2.9 and 3.3–3.7 ppm as shown in Figure 2.5. The shift around 2.3 –2.9 ppm was due to the presence of the protons of a saturated carbon atom attached to nitrogen, of –C-N type. The shift around 3.3 –3.7 ppm was due to the presence of functional group of –(‘NR₃) type.

The ester formation in the surfactant LI and the amine addition for the conversion to amphoteric group in DEALI were confirmed clearly from the spectral data.
2.7 Characterisation through surfactant properties

2.7.1 Methods for the characterization of surfactant properties

2.7.1.1 Surface tension and Critical Micelle Concentration (CMC)

Surface tension and critical micelle concentration (CMC) were determined using KRUSS tensiometer K100 (KRUSS GmbH, Hamburg) (Figure 2.6) at ambient temperature by ring balance method\textsuperscript{105} of different concentrations as required.

![Figure 2.6 KRUSS Tensiometer\textsuperscript{106}](image)

2.7.1.2 Contact angle

Contact angle was determined using KRUSS tensiometer K 100 (Figure 2.6) by sorption measurements according to the Washburn method.
2.7.1.3 Surface energy

Surface energy was calculated using Young’s equation. As determination of contact angles over wet leather is difficult to measure, these experiments were performed on two different surfaces. i.e., extremely hydrophobic (teflon) and extremely hydrophilic (glass). At a particular concentration, surface tension and contact angle were measured as per the details given under sections 2.7.1 and 2.7.2. From the values, surface energy was calculated as a product of surface tension and cos value of the contact angle.

2.7.1.4 Emulsification power

Emulsification power was determined as the separation time measurement. 1% solution of the sample was prepared using distilled water. 40ml of the solution was mixed with 40ml of light liquid paraffin. Ten downward strokes were given. The separation time for the aqueous layer of 10ml and 20ml noted as emulsification power.

2.7.1.5 Zeta Potential

Zeta potential was measured using Zetasizer 2000 (Figure 2.7), model DTS 5202, from M/s Malvern Instruments Limited, UK.
2.7.1.6 Particle size

Particle size of the surfactants were measured using spectrex laser particle counter (Figure 2.8), (PC-2200\textsuperscript{8}), size range 1-100 microns.
2.7.1.7 Isoelectric point

IEP was measured using precalibrated standard LABINDIA make pH meter. The surfactant pH was initially checked and added with dilute acetic acid for pH reduction. At a particular pH, solubility of the surfactant in water becomes lowest and got precipitated out. The pH at which precipitation occurred was measured and reported as isoelectric point.

2.7.2 Surfactant characterisation

The surfactant properties such as CMC, contact angles (Glass and Teflon), surface energy (Glass and Teflon) and emulsification power of LI and DEALI were given in Table 2.2. Zeta potential, particle sizes and IEP of LI and DEALI were given in Table 2.3.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC (mol/L)</th>
<th>Contact angle</th>
<th>Surface energy (mN/M)</th>
<th>Emulsification power of 1% solution (Time in sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI</td>
<td>0.01672</td>
<td>20º 45º</td>
<td>23.2 17.5</td>
<td>155 366</td>
</tr>
<tr>
<td>DEALI</td>
<td>0.00168</td>
<td>20º 45º</td>
<td>22.5 16.9</td>
<td>224 461</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Zeta potential (mv)</th>
<th>Particle size (Microns)</th>
<th>IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI</td>
<td>-64.1</td>
<td>Min Max Mean</td>
<td>pH</td>
</tr>
<tr>
<td>DEALI</td>
<td>+20.1</td>
<td>37 92 57</td>
<td>4.8</td>
</tr>
</tbody>
</table>
The effect of concentration on surface tension of LI and DEALI were shown in Figure 2.9.

Figure 2.9 – Surface tension at different concentrations of anionic LI and amphoteric DEALI
Average particle counts of LI and DEALI were shown in Figure 2.10 and 2.11.

**Figure 2.10 – Average particle count of anionic LI**

**Figure 2.11 – Average particle count of amphoteric DEALI**
Particle size distribution analysis (Minimum, maximum and mean sizes of particles) of LI and DEALI were shown in Figure 2.12.

**Figure 2.12** – Size distribution analysis of LI and DEALI
2.8 Behaviour of surfactant properties

2.8.1 CMC

From the CMC results for LI and DEALI in Table 2.2, it was very clearly understood that the value of the amphoteric surfactant was almost 10 folds lesser than that of anionic surfactant. The reason can be attributed to the longer chain length of the carbon atoms in the amphoteric surfactant, which resulted in increased hydrophobicity. As a result, the amphoteric surfactant had a tendency to aggregate and form a micelle in lower concentrations. Coexistence of functional groups in the molecular structure influenced the colloidal property of the surfactants.109

2.8.2 Contact angle

Contact angle measurements were used to quantify the behaviour of surfactants in contact with the solids and the formation of droplets as formed by the liquid-liquid and liquid-solid interfaces. This was measured for the surfactants at hydrophobic surface (Teflon) and hydrophilic surface (Glass). In the present study, the values of both the surfactants on both the surfaces were found to have same values. In both the cases, the surfactant tends to spread out over the surface.
2.8.3 Surface energy

Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is created. The surface energy may be defined as the excess energy at the surface of a material compared to the bulk.

It is the interaction between the forces of cohesion and the forces of adhesion which determines whether or not wetting, the spreading of a liquid over a surface, occurs. If complete wetting does not occur, then a bead of liquid will form, with a contact angle which is a function of the surface energies of the system. Young’s equation gives the following relation:

\[ \gamma_{SL} + \gamma_{LV} \cos \theta_c = \gamma_{SV} \]

where \( \gamma_{SL} \), \( \gamma_{LV} \), and \( \gamma_{SV} \) are the interfacial tensions between the solid and the liquid, the liquid and the vapour, and the solid and the vapour as shown in Figure 2.13.

![Young’s surface energy model](image)

*Figure 2.13 – Young’s surface energy model*
The equilibrium contact angle that the drop makes with the surface is denoted by $\theta_c$. The difference between $\gamma_{SV}$ and $\gamma_{SL}$ indicates the spreading or wetting of liquid on the surface. The higher value of this term indicates the surface prefers to be wetted by the liquid.

The determination of contact angles over wet leather was not feasible and also the fact that the leather contains both hydrophilic and hydrophobic regions. Therefore, these experiments were performed on two different surfaces having extremely hydrophobic (Teflon) and extremely hydrophilic (Glass) surfaces. The important characteristics of a liquid surfactant is its ability to freely wet the surface of the object being experimented and also to fill the void\textsuperscript{111}. Surface energy was quantified in terms of the forces acting on a unit length at the solid-air or the solid-liquid interface.

Surface energy of the surfactant is the difference of surface tension of solid to vapour and solid to liquid which is equal to surface tension of liquid to vapour multiplied by the cos value of the contact angle, all at a particular concentration.
In the present study, we have calculated the surface energy of both the anionic and amphoteric surfactants using the surface tension of the surfactant at 0.5% concentration and the measured contact angles on teflon and glass surfaces at the same concentration. There was not much variation observed on both the surfaces for both the surfactants. Hence, wetting capability of both the surfactants were same under similar conditions.

2.8.4 Emulsification power

Emulsification power is the capacity of a surfactant to retain the oil portion to a maximum possible extent and depends on the surface activity. In the present study, it was clearly observed from Table 2.2 that the higher emulsification capacity as expected for the amphoteric surfactant. In the case of 10 ml separation, retention time was 45% more in amphoteric surfactant and for 20ml separation, time increased by 26%. The tighter and the closer packing of the hydrophobic groups of the surfactant at the interface results in a more cohesive and stable interfacial film\textsuperscript{112} resulting in the higher emulsification power. The hydrophobicity of amphoteric surfactant migrated the micelle to the air/water interface. The surfactants with the higher emulsification property, besides having the property of being able to emulsify and disperse fats and oils, possess better capacity of binding to leather collagen through electrostatic and hydrophobic interactions.
2.8.5 Zeta potential

Zeta Potential is the potential difference between the medium and the stationary layer of fluid attached to the dispersed particle. The value of zeta potential, measured in millivolts, can be related to the stability of colloidal dispersions.

In the present study, zeta potential of LI and DEALI were found to be -64.1 and +20.1 mv respectively. The values of LI and DEALI indicated potential stability. In particular, DEALI was found to be stable across the whole pH range and impart stability to other surfactant systems. Interestingly, the emulsion from DEALI was found to be stable even in hard water and this property is a critical parameter of a surfactant. CMC of LI and DEALI were found to be 0.01672 and 0.00168 mol/L respectively. Zeta potential value indicated the lowering of CMC so as to make easier aggregation of micelles.

2.8.6 Particle size

Mean particle size of LI and DEALI surfactants were found to be 13 and 57 microns respectively as shown in Table 2.3 and Figure 2.12. Average particle counts were given in Figures 2.10 and 2.11. Normally lower particle size species was preferred choice for the effective application. In addition, the performance of the surfactant depends on solubility, emulsion stability and interfacial tension also.
2.8.7 IEP

A remarkable characteristic\textsuperscript{113} of amphoteric surfactant was the isoelectric point and this was absent in the other surfactant. IEP of DEALI was found to be 4.8, where the solubility was the lowest.

2.8.8 Surface tension at different concentrations

From the results of surface tension at different concentrations, it was clearly observed that the lowering of surface tension was higher in the case of amphoteric surfactant than in anionic surfactant in the entire concentration range that was tested. At higher concentrations, the difference of surface tension of anionic and amphoteric surfactants were comparatively lower, whereas at lower concentrations, the surface tension was found to be higher.

The difference in the surfactant activity depends on the efficiency of adsorption at the interface. In the case of amphoteric surfactant, the efficiency of adsorption at the interface was found to be higher than in the anionic surfactant.

Also, the packing in the amphoteric surfactant increases surface activity due to the increase in the number of carbon atoms in the hydrophobic group. This resulted in excellent hydrotropic properties.
From the results of lowering of surface tension, it was observed that the amphoteric surfactant were more effective in reducing surface tension at lower concentrations.

2.9 Application of the amphoteric surfactant as fatliquors

Fatliquors were prepared by blending a mixture of vegetable oil (12.5%), mineral oil (10%), chloroparaffin sulfonate (22.5%) and surfactant (20%). The composition was adjusted to 100 % using water.

The surfactants used were anionic surfactant, namely lauryl itaconate in the first fatliquor (FL 1) and the amphoteric surfactant, namely diethylamino-lauryl itaconate in the second fatliquor (FL 2). FL 1 and FL 2 were analyzed for colour, clarity, % water, pH and emulsion stability. Colour in lovibond gardener scale found to be 12 with clear clarity. % Water and pH were 35.0 and pH respectively. Fatliquors using hard water emulsions prepared upto 2000 ppm of calcium chloride were stable.

2.9.1 Methods for the characterization of fatliquor properties

2.9.1.1 Colour and clarity

Colour was measured using Lovibond Tintometer – PFX 195 Model as shown in Figure 2.14. Clarity was visually seen and reported.
2.9.1.2 Stability of emulsions

2% Calcium chloride solution was prepared and kept as a standard stock (20,000ppm solution). The stock solution was diluted to the required hardness level. 10 ml of the sample was taken and added with 90 ml of the prepared hard water. The nature of the emulsion was checked.

2.9.2 Fatliquoring process

The fatliquors FL 1 and FL 2 were applied on wet blue cow leather against each other. The general leather fatliquoring process set up and the process were given in Figure 2.15 and Table 2.4.
Figure 2.15 – Leather fatliquoring process set up
### Table 2.4 - Leather fatliquoring process

<table>
<thead>
<tr>
<th>Products</th>
<th>% Used</th>
<th>Duration in minutes</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetting agent</td>
<td>1.0</td>
<td>30</td>
<td>Drain / Wash / Drain</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.75</td>
<td>20</td>
<td>Check pH (3.2)</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td></td>
<td>Drain out</td>
</tr>
<tr>
<td>Basic chromium sulphate</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrome syntan</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fat emulsion</td>
<td>0.25</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Sodium formate</td>
<td>1.0</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>1.0</td>
<td>30</td>
<td>Check pH (4.0)</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Neutralisation agent</td>
<td>2.0</td>
<td></td>
<td>Check pH 5.2, Drain / Wash / Drain</td>
</tr>
<tr>
<td>Sodium formate</td>
<td>1.0</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>1.0</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td><strong>LHS</strong> – Fatliquor 1 &amp; <strong>RHS</strong> – Fatliquor 2</td>
<td>8.0</td>
<td>60</td>
<td>Check exhaustion</td>
</tr>
<tr>
<td>Formic acid</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Drain / Wash / Pile over night / Next day single setting / Hook to dry / Stake

**LHS:** Left Hand Side of leather and **RHS:** Right Hand Side of leather
2.10 Performance evaluation

2.10.1 Assessment of leathers

2.10.1.1 Organoleptic properties

Quality of leathers will be usually assessed by pulling, stretching, rolling, folding with the hands. The other body organs like eyes, nose and ears were also used for leather quality assessment and hence called as organoleptic parameters (Figure 2.16).

The parameters such as feel, softness, grain touch, stretch and bleaching were measured visually by different qualified leather technologists qualitatively and standard deviation was used for averaging out the results. These were measured on the scale of 0 – 5.

Scale of grading

1.0. Very poor
2.0 Poor
3.0 Good
4.0 Very good
5.0 Excellent
2.10.1.2 Tensile strength

Tensile strength is the force required to rupture a leather specimen of unit cross sectional area. It was measured using PROLIFIC tensile strength machine model no TEL 500 (Figure 2.17).
Figure 2.17 PROLIFIC tensile strength machine

2.10.1.3 Grain and bursting strengths

Grain and bursting strengths are the pressures required to cause first sign of crackiness on the grain and for the burst of the leather. The parameters were measured through PROLIFIC lastometer (Figure 2.18).
2.10.2 Properties of leathers

Wet blue cow leathers treated with the prepared fatliquors FL 1 against FL 2 were evaluated qualitatively and quantitatively. Detailed results were given in Table 2.5.
Table 2.5 – Properties of leathers treated with FL 1 against FL 2

<table>
<thead>
<tr>
<th>Properties</th>
<th>FL 1</th>
<th>FL 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softness</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Touch</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Dye brilliance and evenness</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>Tensile strength (Kg/cm²)</td>
<td>286.0</td>
<td>381.0</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>4.0</td>
<td>4.2</td>
</tr>
<tr>
<td>% Elongation</td>
<td>33.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Bursting strength (Kg/cm)</td>
<td>No bursting</td>
<td>No bursting</td>
</tr>
<tr>
<td>Distention (mm)</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Comparison of resultant leathers made from of fatliquors with LI and DEALI. DEALI showed very clearly the better performance of fatliquor prepared from the amphoteric surfactant. Softness and touch of the leather of DEALI showed 12.5% increase during qualitative assessment. Dye brilliance and evenness were better on comparison with the leather of LI. Tensile strength of leather treated with DEALI was increased by 33.0%, whereas, there was no difference in bursting strength.

Treated leather samples were enclosed in the end of the thesis.
The reasons for the increased performance can be attributed to the activity and stability of the amphoteric surfactant. The possible reason was that a higher activity surfactant in a fatliquor avoids the deposition of neutral oil on the leather surface which will result in lowering of softness. Lower emulsion stability of LI when compared to DEALI resulted in the deposition of neutral oil on the leather surface and softness was reduced. Fatliquor with higher emulsion stability primarily depends on the surfactant activity was penetrating well into the leather and splitting up of fibers happened yielding better softness. Higher tensile strength was due to the higher stability of the surfactant.

Leather softness was normally achieved by the addition of surfactants as fatliquors which should be penetrative. Solubility of DEALI was better than LI to form a stable emulsion and also over a wide range of pH. The emulsion was broken within the fibre structure, either by the reactive surfactant interacting with the charged substrate or through protonation by solution pH reduction to change HLB balance. Stable emulsion of DEALI produced good absorption and increased the penetration. In the case of FL 2, the surfactant DEALI besides having the property of being able to emulsify and disperse the fats and oils, possessed the capacity of binding to proteins through electrostatic and hydrophobic interactions.
Softness and touch of the resultant leather treated with FL 2 was better because of the presence of cationic nitrogen group, which makes leather fibres softer or helped the leather for good absorption of fatliquor. In addition, the formation of hydrogen bonding and ionic bonding, and also the molecular weight of the system had some effect on the performance. The carboxylic group of the amphoteric surfactant can form chelate ring with the chrome on the leather. As a result, it can exert a strong action on leather through its physical and chemical interactions with the collagen fibres. This implies that the cross-linking density of collagen fibres improves after tanning and that the carboxyl groups play an important role in the tanning process.

In addition to better performance towards softness and touch, we could also observe a drastic difference in dye brilliance and evenness in the case of FL 2. The amphoteric surfactant present in FL 2 improved the surface dye colour yield and evenness because of the cationic group of DEALI attracts anionic dyestuffs through electrostatic coupling\textsuperscript{118}.

On the other hand, in the case of LI, the anionic surfactant could lower the positive potential of chrome tanned leather which has disadvantageous effects for the combination between anionic dyestuffs and leather.
2.10.3 Scanning electron microscopic (SEM) analysis

The resultant leathers after fatliquoring and drying were spin coated with gold. JEOL 400 microscope was used for SEM analysis. SEM studies of grain pattern of leathers fatliquored with FL 1 and FL 2 were shown in Figures 2.19 and 2.20, at a magnification of X 2000.

Figure 2.19 – SEM photograph of resultant leather treated with fatliquor FL1 prepared using anionic surfactant LI at a magnification of X 2000
Figure 2.20 – SEM photograph of resultant leather treated with fatliquor FL2 prepared using amphoteric surfactant DEALI at a magnification of X 2000

Fibre splitting was clearly observed in Figure 2.20, DEALI based fatliquor FL 2 penetrated deeply resulting in well fiber splitting and yielded better softness due to higher stability.
2.11 Conclusions

An anionic polymerisable surfactant lauryl itaconate (LI) was synthesized. This was reacted with diethylamine to prepare a new amphoteric surfactant, diethylamino-lauryl itaconate (DEALI). LI and DEALI were characterized by FT-IR and $^1$H NMR spectra. The surface tension at different concentrations, critical micelle concentration, contact angles measured on hydrophilic and hydrophobic surfaces (Glass and Teflon), surface energy (Glass and Teflon), emulsification power, zeta potential and particle size properties of LI and DEALI were measured.

The amphoteric surfactant DEALI was tested against the anionic polymerisable surfactant LI as a control as fatliquors on wet blue cow leather. Qualitative assessment of leathers showed an increase of 12.5% in softness and touch in the case of amphoteric surfactant. Tensile strength improved by 33%. The improvement in the properties was due to the higher surfactant activity providing stable emulsion, good solubility and stability of the surfactant over the wide pH range. Dye brilliance and evenness was better in the case of amphoteric surfactant due to the presence of cationic group through electrostatic coupling with the anionic dyestuffs.