

PREPARATION OF A NEW ITACONATE BASED AMPHOTERIC SURFACTANT FOR FATLIQUOR APPLICATIONS

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ABSTRACT

Amphoteric surfactant based fatliquors are outstanding performers in the leather industry because of their excellent surfactant properties, low toxicity, good biodegradability, excellent resistance to hard water, antistatic properties, good emulsification, dispersion and compatibility with other agents. This paper reports on the preparation of a new amphoteric surfactant, diethylamino-lauryl itaconate (DEALI) through the synthesis of lauryl itaconate (LI) based anionic polymerisable surfactant (“Surfmer”). DEALI and LI were characterized by FT-IR and ¹H NMR spectra. Properties of both DEALI and LI such as surface tension at different concentrations, critical micelle concentration, contact angle, surface energy, emulsification power, zeta potential and particle sizes were measured. The Isoelectric Point (IEP) of DEALI was determined. The amphoteric surfactant (DEALI) and the anionic surfactant (LI) were formulated as fatliquors and applied on wet blue cow leather, against each other. Fatliquor imparted properties on the leather were measured qualitatively and quantitatively. Scanning Electron Microscopic studies of the resultant leather was carried out and found to have better performance due to deeper penetration of the amphoteric surfactant. This work provides a lead for the development of new and better fatliquoring agents.

RESUMEN

Engrasantes basados en tensoactivos anfóteros se destacan en la industria del cuero debido a sus excelentes propiedades surfactantes, baja toxicidad, buena biodegradabilidad, excelente resistencia al agua dura, propiedades antiestáticas, buena emulsificación, dispersión y compatibilidad con otros agentes. Este documento informa sobre la preparación de un nuevo agente tensoactivo anfótero, dietilamino-lauril itaconato (DEALI) a través de la síntesis de itaconato lauril (LI), basado en un surfactante polimerizable aniónico (“Surfmer”). DEALI y LI se caracterizaron por FT-IR y espectro ¹H NMR. Las propiedades de ambos DEALI y LI, tales como la tensión superficial a diferentes concentraciones, concentración micelar crítica, ángulo de contacto, energía superficial, poder emulsionante, el potencial zeta y el tamaño de partículas fueron medidos. El Punto Isoeléctrico (IEP) de DEALI fue determinado. El surfactante anfótero (DEALI) y el surfactante aniónico (LI) se formularon como engrasantes y se aplicaron a cuero bovino en wet blue, uno contra el otro. Las propiedades impartidas por el engrasante al cuero fueron medidos cualitativa y cuantitativamente. Estudios de Microscopía de Barrido Electrónico de la piel resultante se han llevado a cabo y se encontró que tienen un mejor rendimiento debido a una penetración más profunda del tensoactivo anfótero. Este trabajo proporciona una ventaja para el desarrollo de nuevos y mejores agentes engrasantes.

INTRODUCTION

Organized self-assembled surfactant phases have received a lot of attention recently as possible viable reaction and templating media. However, conventional surfactant structures are of limited use due to their dynamic nature. Polymerizable surfactants¹ ('surfmers'), on the other hand, offer potential for developing hybrid nanosized reaction and templating media with constrained geometries. Surfmers have been developed for enhancing kinetic and or mechanical stability of molecular assemblies in aqueous solutions.² 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.³ Amphoteric surfactants prepared through the route of synthesis of polymerizable surfactants have received considerable attention because of their extensive industrial applications, in particular leather processing as fatliquors. They show high emulsion stability to salts responsible for the hardness of water, as well as to alkali salts. In the fatliquoring of leather and skins, they give pleasantly soft, lardy and supple feel after thorough application to leather.⁴ Dye finishes are distinguished by evenness and brilliance. In the case of suede type leathers, a silky nap with an attracting scribing effect was obtained. By virtue of the amphoteric character, the surfactants can be formulated along with cationic, anionic and also nonionic ingredients during the preparation of a fatliquor. The main purpose of fatliquoring is to prevent the final product having a thin and dry handle and to minimize fibril adhesion during drying.⁵

The conjugate addition of nucleophiles to electron-deficient alkenes is an important reaction and has wide applications in organic synthesis.⁶ The addition of amines to α,β -unsaturated carbonyl compounds particularly produce the β -amino derivatives that are useful intermediates in the synthesis of a large number of products with a wide range of biological activity. Synthesis of a number of amphoteric surfactants and its application on leather as a fatliquor, through various methods reported in the literature.⁷⁻¹⁸ Recent research shows the development of quite a number of amphoteric fatliquors.¹⁹⁻²⁷ 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.²⁸ However, there are no reports on the conjugate Michael addition of an amine to a polymerizable surfactant having α,β -unsaturated carbonyl group to yield an amphoteric surfactant and the development of fatliquor for leather processing to the best of our knowledge.

In the present research, we have reported a preparation of a new amphoteric compound diethylamino-lauryl itaconate (DEALI), through the conjugate Michael addition of an amino group, diethylamine to a polymerizable anionic surfactant lauryl itaconate (LI) having α,β -unsaturated carbonyl group,

synthesized by the esterification of lauryl alcohol and itaconic acid. Itaconic acid has been extensively studied with regard to its polymerization kinetics, role of bulky substituents, chain stiffness and glass-transition temperatures. Being a polymerizable dicarboxylic acid, it has the potential of being readily derivatized to generate polymerizable surfactants.³ DEALI and LI were characterized spectroscopically. Several properties of DEALI and LI were measured, Isoelectric Point of DEALI was determined. Fatliquors were separately prepared using DEALI and LI. The properties imparted to leather by the surfactants were evaluated.

EXPERIMENTAL

Materials

Lauryl alcohol, itaconic acid, para toluene sulphonic acid, sodium hydroxide, diethyl amine were used as laboratory reagent (LR) grade without any further purification. Vegetable oil, mineral oil, chloroparaffin sulfonates and neutralization agent were industrial grade products.

Experimental Methods

Fatliquors were prepared in two stages. In the first stage, the amphoteric surfactant was synthesized through the synthesis of polymerizable anionic surfactant followed by the formulation as fatliquors in the second stage.

1. (a) Synthesis of LI polymerisable anionic surfactant:

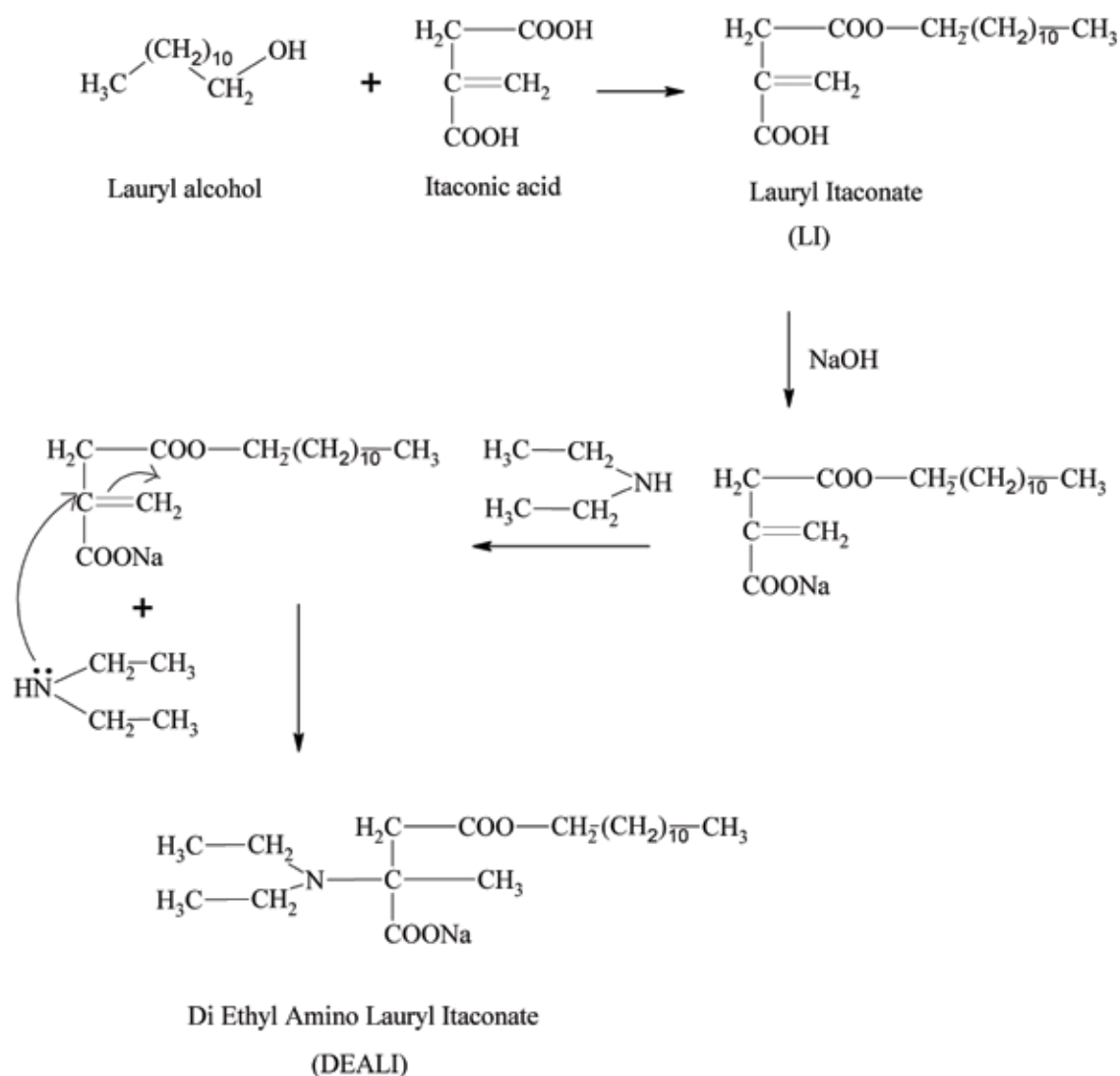
1 mole (186g) of lauryl alcohol was heated for 15 min. at 105°C to remove moisture present, followed by the addition of 1 mole (130g) of itaconic acid and 1% of para toluene sulphonic acid (3.2g). The temperature of the oil bath was heated to 115 ± 5° C and maintained for 4h. The drop in the acid value was checked to make sure that the reaction was completed. After the completion of the esterification, pH was adjusted to 8.0 using sodium hydroxide.

(b) Synthesis of DEALI amphoteric surfactant:

1 mole (298g) of LI was added to 1 mole (73g) of diethylamine, slowly over a period of 30 min. at room temperature. Reactants were stirred at 30-32°C as a neat mixture⁶ for 5h. The chemical reactions and the structures of LI and DEALI were shown in Scheme 1.

2. Preparation of fatliquors and their application on leather

Fatliquors were prepared by taking a mixture of vegetable oil (12.5%), mineral oil (10%), chloroparaffin sulfonate²⁹ (22.5%) and surfactant (20%). The composition was adjusted to 100 % using water. The surfactants were anionic surfactant (LI) in the first fatliquor (FL 1) and the amphoteric surfactant (DEALI) in the second fatliquor (FL 2). The fatliquors FL 1 and FL 2 were applied on wet blue cow leather against each other.



Scheme 1. Synthesis of LI and DEALI

Characterization Methods

The measure of acid value, % water content and pH were determined using standard analytical methods. Acid value and % water content were carried out as per IS:548:1964.³⁰ pH and IEP were measured using precalibrated standard LAB INDIA make pH meter. FT-IR spectrum was taken using KBr pellet on BRUKER, IFS, 66V FT-IR spectrometer. ¹H NMR spectrum was taken using CDCl₃ as a solvent using JEOL GSX 400, NB FT NMR spectrophotometer. Surface tension and critical micelle concentrations (CMC) were determined using KRUSS tensiometer K100 (KRUSS GmbH, Hamburg) at ambient temperature by ring balance method³¹. Contact angles were determined using KRUSS tensiometer K 100 by sorption measurements according to the Washburn method³². Surface energy was calculated using Young's equation.³³ Emulsification power was determined as the separation time measurement.³⁴

Zeta potential was measured using Zetasizer 2000, model DTS 5202, from M/s Malvern Instruments Limited, UK. Particle size of the surfactants was measured using spectrex laser particle counter, (PC-2200^R), size range 1-100 microns. Color of the fatliquors were measured with Lovibond PFX 195 Tintometer. The fatliquoring process adopted and the experimental details were given in Table I. The physical properties of resultant leathers were measured using standard methods. Scanning Electron Microscopic (SEM) studies of the dried leather samples were carried out using JEOL 400 microscope after spin coated with gold.

RESULTS AND DISCUSSION

Analytical Characterization of Surfactants

The preparation of DEALI was carried out in two steps. The first step was the esterification of itaconic acid and was carried

TABLE I
Leather Fatliquoring Process

Products	% Used	Duration in minutes	Remarks
Water	100		
Wetting agent	1.0	30	Drain / Wash / Drain
Water	100		
Formic acid	0.75	20	Check pH (3.2)
			Drain out
Water	100		
Basic chromium sulphate	4.0		
Chrome syntan	2.0		
Fat emulsion	0.25	60	
Sodium formate	1.0	10	
Sodium bicarbonate	1.0	2 equal feeds at the interval of 10 minutes and run for 30 minutes	Check pH (4.0)
			Drain / Wash / Drain
Water	100		
Neutralisation agent	2.0	30	
Sodium formate	1.0	10	
Sodium bicarbonate	1.0	2 equal feeds at the interval of 10 minutes and run for 30 minutes	Check pH 5.2 ,
			Drain / Wash / Drain
LHS : RHS			
FL 1 : FL 2	8.0	60	
Formic acid	1.5	2 equal feeds at the interval of 10 minutes and run for 30 minutes	Check exhaustion
			Drain / Wash / Drain/
			Pile over night/ Next day single setting,
			Hook to dry, Stake.

LHS: Left Hand Side , RHS: Right Hand Side

out at $115 \pm 5^\circ\text{C}$ by checking the drop in acid value till it becomes consistent (166). Acid value during the second hour was 220. Acid values after 3 and 4 hours were found to be 169.7 and 166 respectively. The ester was neutralized to the pH of 8.0 using sodium hydroxide. Diethylamine was reacted during the second step at $30\text{--}32^\circ\text{C}$ for 5 hours. After the completion of the reaction, % water and pH were analyzed as 18.0 and 12.5 respectively. Final pH adjusted to 7.0 using formic acid.

FTIR Characterization

The IR spectra³⁵ of DEALI was shown in Figure 1.

Common peaks at 2955, 2852, 1737, 1466, 1241, 1180 and 721 cm^{-1} observed for LI and DEALI, due to different types of stretches of common groups. Characteristic peaks observed for LI at 947 and 866 cm^{-1} were due the presence of aliphatic unsaturation of the type $\text{CH}_2=\text{CHOCOR}$. 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 in 1351 and 771 cm^{-1} due to the deformation of $-\text{C}-\text{N}-\text{C}$ 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.

¹H NMR Characterization

The ¹H NMR spectra³⁶ of LI and DEALI were shown in Figures 2 and 3.

The common functional groups present in LI and DEALI were found to have the same chemical shifts as illustrated in the figures. The shifts at 0.9 and 1.28 ppm were due to the presence of SP^3 hybridized protons (C-H's) of saturated carbon atoms of lauryl (CH_3 type) group of the surfactants. The chemical shift at 4.1 ppm was due to the presence of ester group of type $-(\text{OCOR})$. This shift occurred due to oxygenated SP^3 hybridized protons (C-H's) of ester functional group. The characteristic chemical shift of LI at 4.8 ppm is due the presence of protons of aliphatic unsaturation of the type ($\text{CH}_2=\text{CH}-$). During the conversion to amphoteric surfactant, the double bond got saturated with the addition of nucleophile. Hence, the shift at 4.8 ppm disappeared in DEALI. The chemical shifts corresponding to DEALI were present at 2.3 – 2.9 and 3.3 – 3.7 ppm. as shown in Figure 3. 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 $-\text{C}-\text{N}$ type. The shift around 3.3 – 3.7 ppm was due to the presence of functional group of $-(^+\text{NR}_3)$ 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.

Surfactants Properties

The CMC, contact angle (Glass), contact angle (Teflon), surface energy (Glass), surface energy (Teflon) emulsification power, zeta potential, particle size properties of LI and DEALI were given in Table II along with the isoelectric point of DEALI.

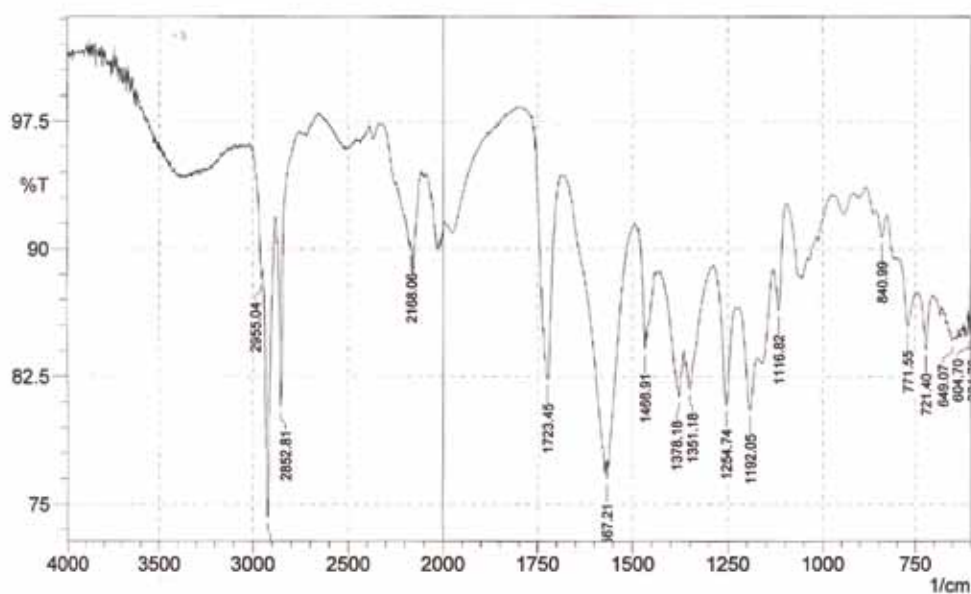


Figure 1. IR spectra of DEALI

Surface tension at different concentrations and average particle counts of LI and DEALI were shown in Figure 4 and 5.

From the results of surface tension at different concentrations, it was very clear that the lowering of surface tension was larger in the case of amphoteric surfactant than in anionic

surfactant in all the concentrations. At higher concentrations, the difference of surface tension of anionic and amphoteric surfactants were comparatively smaller, whereas at lower concentrations, the surface tension was found to be larger. Difference in the surfactant activity depends on the efficiency of adsorption at the interface. In the case of amphoteric

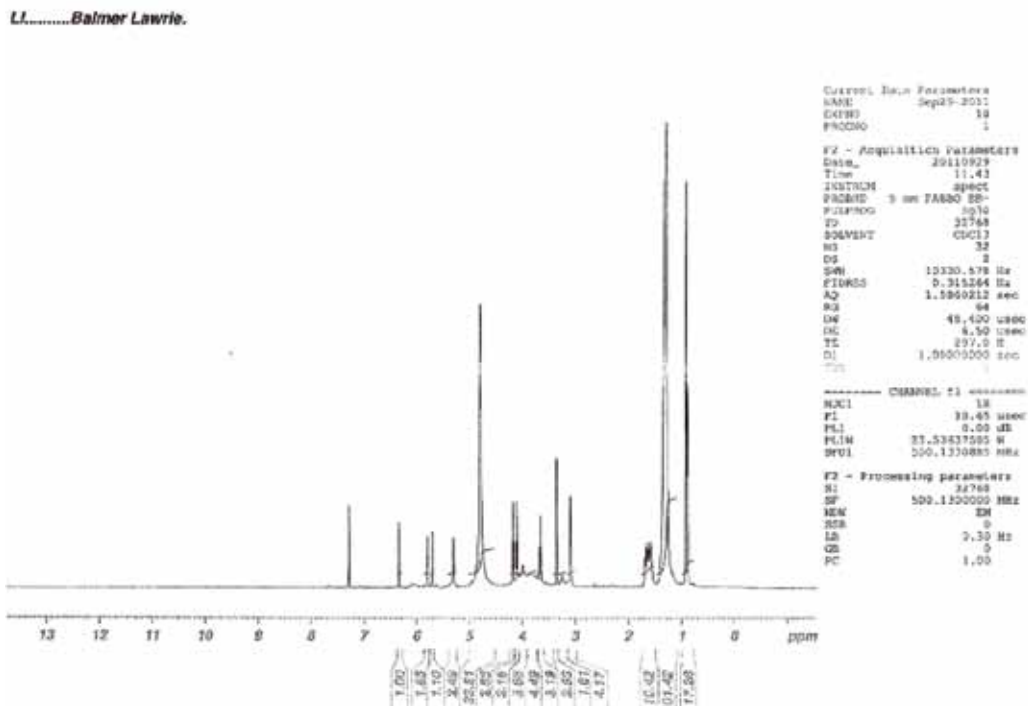


Figure 2. NMR spectra of LI

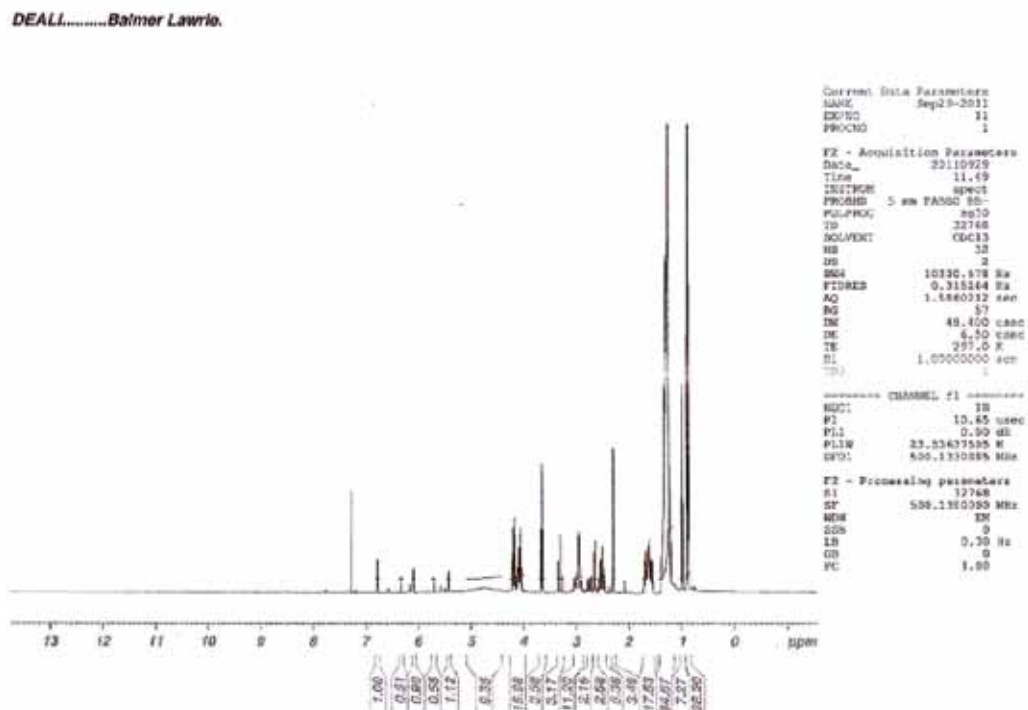


Figure 3. NMR spectra of DEALI

surfactant, the efficiency of adsorption at the interface was found to be larger than in the anionic surfactant. Also the packing in the amphoteric surfactant increases surface activity³⁷ 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 was more effective in reducing surface tension at lower concentrations.

From the CMC results for LI and DEALI in Table II, it was very clearly understood that the value of the amphoteric surfactant was almost 10 folds lesser than that of anionic

TABLE II
Surfactant Properties

Surfactant	CMC (mol/L)	Contact angle		Surface energy (mN/M)		Emulsification power of 1% solution (Time in sec)		Zeta Potential (mv)	Particle Size (Microns)			IEP pH
		Glass	Teflon	Glass	Teflon	10ml	20ml		Min	Max	Mean	
LI	0.01672	20°	45°	23.2	17.5	155	366	-64.1	7	42	13	-
DEALI	0.00168	20°	45°	22.5	16.9	224	461	+20.1	37	92	57	4.8

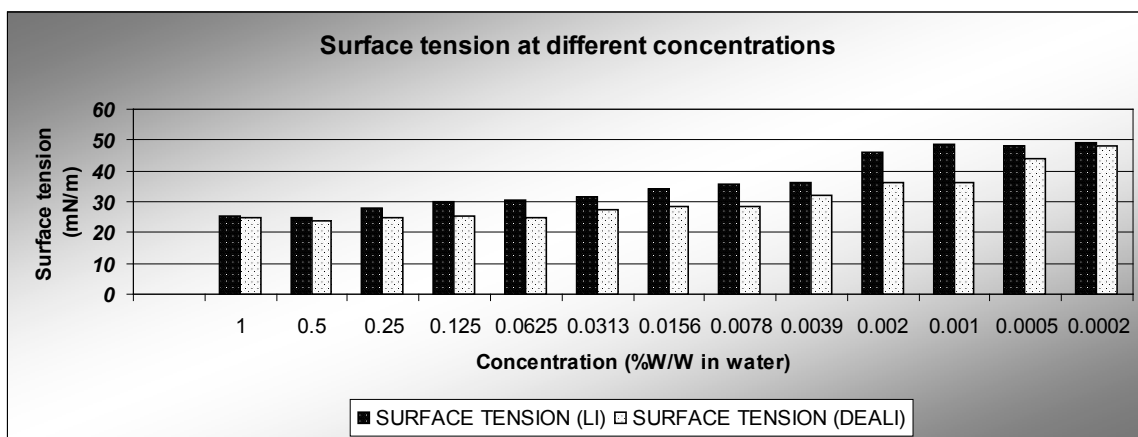


Figure 4. Surface tension at different concentrations of anionic LI and amphoteric DEALI

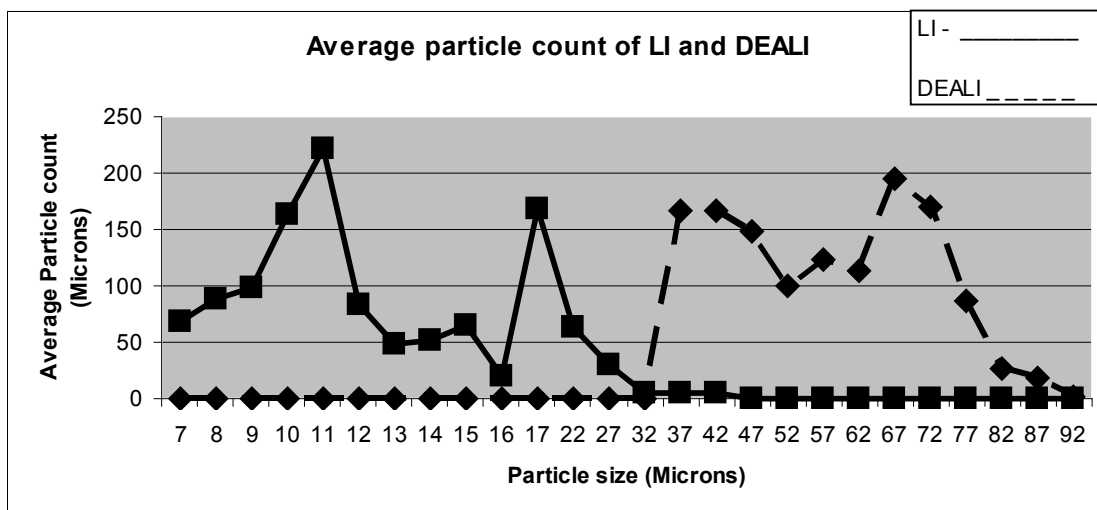


Figure 5. Average particle count of LI and DEALI

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.³⁸ Contact angle was 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). Studies and measurements of contact angles of liquids on solids have great technological importance.³⁹ In the present study, the values of both the surfactants on both the surfaces were found to be same. In both the cases, the surfactant tends to spread out over the surface.

Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface was created. This can be referred as surface wetting capability⁴⁰. 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 angle on Teflon and glass surfaces at the same concentration, using the following Young's equation.

$$\gamma_{SL} + \gamma_{LV} \cos \theta_c = \gamma_{SV}$$

where γ_{SL} , γ_{LV} and γ_{SV} are the interfacial tensions between solid-liquid, liquid-vapour and solid-vapour respectively. The equilibrium contact angle that the drop makes with the surface was denoted by θ_c . 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.

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, from Table II, it was clearly observed 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 result in a more cohesive and stable interfacial film³⁷ 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.

Zeta Potential is the potential difference between the medium and the stationary layer of fluid attached to the dispersed particle, measured in millivolts. When the ions absorbed⁴¹ on a particle in a colloidal system, or by the dispersed liquid in an emulsion, the charge of the layer surrounding the particle is altered. This results in a change in the potential difference between the surrounding layer of ions and the bulk of the surrounding fluid. The degree of ion absorption is related to the stability of colloidal system and hence on zeta potential. Thus, measurement of zeta potential makes possible the control of processes wherein dispersion or agglomeration is important. In the present study, zeta potential of LI and DEALI were found to be -64.1 and +20.1 mv respectively. As the zeta potential is made more, the stability of the system is increased. In the case of LI, the value of -64.1 mv represents sufficient mutual repulsion to result in assured stability. In the case of DEALI, the value of +20.1 mv represents the agglomeration. In this case, the addition of diethylamine group in the molecule of lauryl itaconate is capable of producing mechanical bridging between particles. In the measurements, it was indicated that the potential stability is comparatively lower in the case of DEALI. But still, DEALI was found to be stable across the whole pH range and impart stability to other surfactant systems due to its amphoteric nature.

Interestingly, the emulsion from DEALI was found to be stable even in hard water and this property is a critical parameter of a surfactant to be a part of fatliqour formulation as the most of the tanneries use hard water because of cost factor. 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. Mean particle size of LI and DEALI surfactants were found to be 13 and 57 microns respectively. Normally lower particle size species was preferred choice for the effective application. In the present study, even though LI was having the lesser particle size, performance as a fatliqour on leather was comparatively lower than that of DEALI, which was having slightly higher particle size. The particle size may be just good enough to penetrate into leather. The reason behind this variation is that in addition to particle size, leather performance depends on solubility, emulsion stability and also interfacial tension.

Solubility, stability over the pH range from acidic to alkaline and also lowering of surface tension of DEALI were better than LI, due to its amphoteric nature. Hence as a fatliqour, performance of fatliqour with DEALI was better than LI. A remarkable characteristic⁴² of amphoteric surfactant was 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.

Analytical Characterization of Fatliquors

Prepared fatliquors FL 1 and FL 2 were analyzed for chemical parameters. Color in lovibond gardener scale found to be 12

with clear clarity. % Water was 35.0 and pH was 8.0. Fatliquors using hard water emulsions prepared up to 2000 ppm of calcium chloride were stable.

Resultant Leather Properties

Wet blue cow leathers were treated with the prepared fatliquors using FL 1 against FL 2. After drying, the leathers were evaluated qualitatively and quantitatively. Detailed results were given in Table III.

On comparison of resultant leathers treated with fatliquors, DEALI based fatliquor showed very clearly the better performance than LI based fatliquor. 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 of DEALI was increased by 33.0%, whereas, there was no difference in bursting strength. The reasons for the increased performance can be attributed to the activity and stability of the amphoteric surfactant. The possible reason is that a higher surfactant activity in a fatliquor avoids the deposition of neutral oil on the leather surface⁴³ that 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 of fibers happened yielding better softness. Higher tensile strength is due to the higher stability of the surfactant.

Leather softness is 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 fiber structure, either by the reactive surfactant interacting with the charged substrate or through protonation by solution pH reduction to change HLB balance.⁴⁴ 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.⁴⁵

Softness and touch of the resultant leather treated with FL 2 was better because of the presence of cationic nitrogen group, which makes leather fibers softer or helped the leather for good absorption of fatliquor. In addition, the formation of hydrogen bonding, 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 fibers. This implies

that the cross linking density of collagen fibers 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 color yield and evenness because the cationic group of DEALI can attract anionic dyestuffs through electrostatic coupling.⁴⁶ 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. SEM studies of grain pattern of leathers fatliquored with FL 1 and FL 2 were given in Figure 6 and 7, at a magnification of X 2000. Extent of fiber splitting was comparatively better in SEM of amphoteric surfactant DEALI based fatliquor. It penetrated deeply resulting in better fiber splitting and softness due to higher stability.

TABLE III
Organoleptic Properties of FL 1 / FL 2

PROPERTIES	FL 1	FL 2
Softness	4.5	5.0
Touch	4.5	5.0
Dye brilliance and evenness	Moderate	Good
Tensile Strength (Kg/cm ²)	286.0	381.0
Standard Deviation	4.0	4.2
% Elongation	33.0	16.0
Standard Deviation	1.8	1.4
Bursting Strength (Kg/cm)	No bursting	No bursting
Distension (mm)	12.0	12.0
Standard Deviation	1.4	1.2

Scale of grading: 1: Very Poor, 2: Poor, 3: Good, 4: Very Good and 5: Excellent

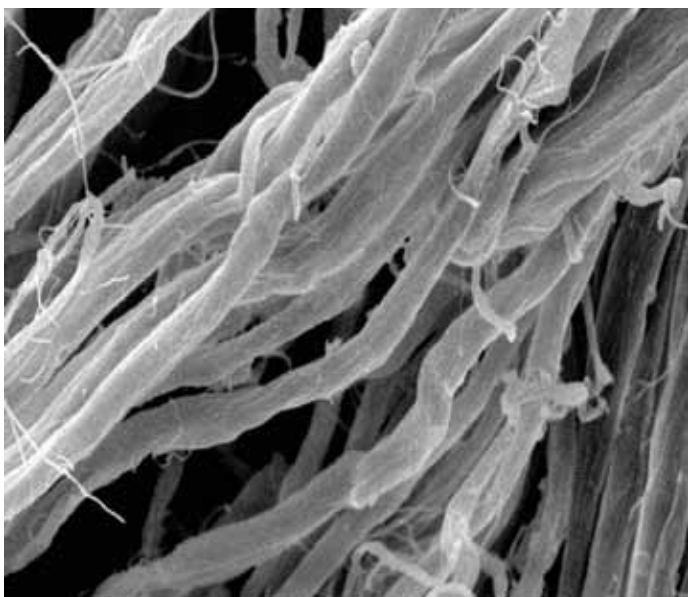


Figure 6. SEM photograph of resultant leather treated with fatliquor FL1 prepared out of anionic surfactant LI at a magnification of X 2000



Figure 7. SEM photograph of resultant leather treated with fatliquor FL2 prepared out of amphoteric surfactant DEALI at a magnification of X 2000

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 ^1H NMR spectra. The surface tension at different concentrations, critical micelle concentration, contact angle, surface energy, emulsification power, zeta potential and particle size properties of LI and DEALI were measured. LI and DEALI were formulated as fatliquors and applied on wet blue cow

leather. Fatliquor imparted properties on the leather were measured. Qualitative assessment of leathers showed an increase of 12.5% in softness and touch by the substitution of amphoteric surfactant. Tensile strength improved by 33%. Improvements were due the higher surfactant activity yielded 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. The present synthesis of amphoteric surfactant yields a better base for the development of high performance fatliquors for the leather industry.

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REFERENCES

1. Mark Summers, and Julian Eastoe; Applications of polymerizable surfactants, *Advances in Colloid and Interface Science* **100 –102**, 137–152, 2003.
2. Kenichi Sakai, Miyuki Wada, Wataru Matsuda, Koji Tsuchiya, Yuichiro Takamatsu, Kazuyuki Tsubone, Takeshi Endo, Kanjiro Torigoe, Hideki Sakai and Masahiko Abe; Polymerisable anionic gemini surfactants: physiochemical properties in aqueous solution and polymerization behavior, *J. of Oleo Science* **58**, 8, 403-413, 2009.
3. Arun Prasath R., and Ramakrishnan S.; Synthesis, characterization and utilization of Itaconate-based polymerisable surfactants for the preparation of surface-carboxylated polystyrene latexes, *J. of Polymer Sci.* **43**, 15, 3257-3267, 2005.
4. Friese Hans herbert, Ploog, Uwe, Uphues, and gunter; *United States Patent*, **4729767**, 1988.
5. Zengin G., and Afsar. A.; Use of natural fat emulsions in fatliquoring process and investigation of fatty spue formation, *JALCA* **106**, 83-90, 2011.
6. Brindaban C.Ranu, Suvendu S.Dey, and Alakananda Hajra; Solvent-free, catalyst-free Michael-type addition of amines to electron-deficient alkenes, *ARKIVOC* (ISSN 1424-6376) (**vii**), 76-81, 2002.

7. Wang Xuechuan, Ding Jianhua, Ding Xiaoli, and Yongqiang; Synthesis of amphoteric phosphate surfactant and its application in leather fatliquoring, *Pige Kexue Yu Gongchen* **18**, 4, 22-25, 2008.
8. Zhao Yongi., Ding Xiuyun., and Cui Yuanchen; Study on synthesis and characteristics of a novel amphoteric fatliquor, *Zhangguo Pige* **34**, 21, 33-36, 2005.
9. Zhao Yangli, and Cui Yuanchen; Study on synthesis and properties of a novel amphoteric fatliquor, *Zhangguo Pige* **33**, 21, 32-35, 2005.
10. Lan Yunjun., and Gu Xuexian; Type, manufacture and its action of the amphoteric surfactants used in leather industry, *Zhangguo Pige* **33**, 9, 10-12, 2004.
11. Wang Xuechuan, and Huarui; Synthesis of amphoteric phosphate and its application on leather fatliquoring, *Pige Huagong* **21**, 6, 16-19, 33, 2004.
12. Lu Shenghua; Synthesis and application of amphoteric fatliquor LDF-II, *Pige Huagong* **20**, 2, 15-18, 2003.
13. Lu Shenghua, and Liang Guozheng; Synthesis and application of amphoteric fatliquor LDF-1, *Pige Huagong* **19**, 15-16, 35, 2002.
14. Lai Yunjun, Yin Dehai, Chen Heng, and Luo Weiping; Preparation and application of ASF-M ampholytic and synthetic fatliquoring agent, *Zhangguo Pige* **29**, 23-25, 2000.
15. Luan Shouting, and Fan Dongyn; Preparation of high-performance combined fatliquor SWG, *Pige Huagong*, **16**, 16-19, 1999.
16. Sun Genxing, Fang Yingsen, Sun Jing, and Lian Peicong; Preparation and application of fatty amidopropyl betaine amphoteric fatliquor, *Zhangguo Pige* **36**, 41-44, 2007.
17. Zheng Shunji, Liu Life, and Ma Hongguang; Synthetic research of new amphoteric fatliquor, *Pige Huagong* **23**, 23-25, 2006.
18. Lan Yunjun, and Gu Xuexian; Type, manufacture and its action of the amphoteric surfactants used in leather industry, *Zhongguo Pige* **33**, 10-12, 2004.
19. Zheng Shunj; Synthesis of alkanolamides of higher fatty acids fatliquoring agent, *Pige Kexue Yu Gongcheng* **21**, 53-56, 2011.
20. Luo Xiaomin, Feng Jienyan, Xie Xing, and Li Pengni; Method for preparing amphoteric lanolin based fatliquoring agent for leather, *Farming Zhuanli Shenqing*, **CN 101864500** A 20101020, 2010.
21. Sun Genxing, Fang Yingsen, Sun Jing, and Lian Peicong.; Preparation and application of fatty amidopropyl betaine amphoteric fatliquor, *Zhongguo Pige* **36**, 41-44, 2007.
22. Lu Shenghua, Sun Genxing, and Yu Congzheng; Synthesis and properties of amphoteric fatliquor, *Zhongguo Pige* **32**, 1-3, 2003.
23. Wang Chen, Cheng Baozhen, Li Shuping, and Li Yanchun; Study on application of amphoteric fatliquor CL-819, *Pige Huogong* **18**, 31-32, 2001.
24. Ma Jianzhong, Lv Bin, Gao Dangge, and Yao Qing; Preparation of polyether type organosilicon modified fatliquoring agent for leather, *Faming Zhuanli Shenqing Gongkai Shuomingsh*, **CN 101532067**, A 20090916, 2009.
25. Wang Xuechaun, Ding Jianhua, Ding Xiaoli, and Ren Yongqiang; Synthesis of amphoteric phosphate surfactant and its application in leather fatliquoring, *Pige Kexue Yu Gongcheng* **18**, 22-25, 2008.
26. Zheng Shunji, and Qiang Xihuai; Preparation and application of amphoteric phosphated fatliquors, *Zhongguo Pige* **35**, 48-51, 2006.
27. Ren Longfang, Wang Xuechuan, Qiang Taotao, and An Huarui; Synthesis of amphoteric phosphate ester surfactant by polyphosphoric acid and its application in free chrome collagen fiber, *Advanced Materials Research* **129-131**, 271-275, 2010.
28. Chen Wang, Shengyu Feng, and Jun Wu; Preparation of organosilicone modified palm oil fatliquor, *JALCA* **106**, 161-169, 2011.
29. Malcolm H. Battles; *Fatliquor practice and theory*, The chemistry and technology of leather, **34**, 90, 1979.
30. Methods of sampling and test for oils and fats; *IS:548:1964*, Part I
31. Rana D, Neale G, and Hornof V.; *J.Colloid. Polym. Sci.* **280**, 8, 775, 2002.
32. Bendure R.; *J. Colloid .Int. Sci.* **42**, 137, 1973.
33. http://en.wikipedia.org/wiki/Surface_energy.
34. Kaurna M.S.L, Reddy J.R.C, Rao B.V.S.K, and Prasad R.B.N.; *J. Surfact. Deter.* **8**, 271-276, 2005.
35. Socrates; *IR handbook*, 1982.
36. Simons W.W.; Ed, Sadtler research laboratories, *The sadtler guide to NMR spectra*, 1983.
37. Hait S.K, and Moulik S.P.; Gemini surfactants: A distinct classs of self-assembling molecules, *Current Science* **82**, 9, 2002.
38. Shuichi Osanai, Go Yamada, and Ruri Hidano; Preparation and properties of phosphate surfactants containing ether and hydroxyl groups, *J. Surfact. Deterg.* **10.1007**, 11743-009-1137-3, 2009.
39. Kanth S.V, Ipe A, Madhan B, Venba R.and Dhathathreyan A.; Effect of different retanning systems on surface properties of leather, *JALCA* **102**, 135-142, 2007.
40. <http://www.ndt-ed.org>.
41. <http://www.zeta-reader.com>.
42. Wang Xuechuan, Qiang Taotao, An Huarui, Ren Longfong, and Zhao Yating; Synthesis of amphoteric phosphate ester fatliquor by polyphosphoric acid and its application in free chrome tanning, China.
43. Zongcai Zhang, Hong Dai, and Juan Du; The effect of fatliquor emulsion on the physical properties of resultant leather, *J. Society of Leather Technologists and Chemists* **88**, 110-112, 2004.

-
44. Covington, and Alexander K.T.W.; The production of soft leather, Part I, The mechanism of chemical softening by lubrication, *JALCA* **88**, 241-253, 1993.
45. Cantera C.S, Garro M.L, Goya L, Barbeito C, and Galarza; Hair saving unhairing process: Part 6, Stratum Corneum as a diffusion barrier: Chemical-Mechanical injury of Epidermis, *J. Society of Leather Technologists and Chemists* **88**, 121-131, 2004.
46. Jin Liqiang, Liu Zonglin, Sli Qinghua, and Li Yanchun; Synthesis and application of an amphoteric acrylic polyelectrolyte as a retanning agent, *J. Society of Leather Technologists and Chemists* **88**, 105-109, 2004.
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