EFFECT OF SPECIFIC ADDITIVES ON THE DEGREE OF SULFONATION AND ITS INFLUENCE ON LEATHER FATLIQUORING

by

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ABSTRACT

Sulfosuccinate type anionic surfactants are classical ingredients for industrial applications. They are of great interest because of their excellent surfactant properties. Fatliquors prepared from sulfosuccinates have been effectively utilized in the leather industry, where the degree of sulfonation of the surfactant plays a crucial role in deciding performance. This paper reports on the study of factors such as the addition of phase transfer catalyst, non-ionic wetting emulsifier and co-solvent on the degree of sulfonation. Emusification power, zeta potential, surface tension and particle size were measured. Reaction conditions were optimized, based on the results. Fatliquors were prepared using different sulfosuccinates and applied on leather. The properties of resultant leathers were studied qualitatively and quantitatively, and SEM studies were carried out for the treated leathers. This work provides a basis for the development of better fatliquoring agents.

RESUMEN

Los tensoactivos aniónicos del tipo Sulfosuccinato son ingredientes clásicos para aplicaciones industriales. Son de gran interés debido a sus excelentes propiedades surfactantes. Engrasantes preparados a partir de sulfosuccinatos se han utilizado eficazmente en la industria del cuero, donde el grado de sulfonación del tensoactivo juega un papel crucial en la decisión de rendimiento. Este documento informa sobre el estudio de factores tales como la adición de un catalizador de transferencia de fase, un emulsionante no iónico humectante y un co-disolvente, en el grado de sulfonación. Poder de emusificación, potencial zeta, tensión superficial y tamaño de partícula fueron medidos. Las condiciones de reacción fueron optimizadas, basadas en los resultados. Los engrases se prepararon utilizando sulfosuccinatos diferentes y se aplicaron sobre cuero. Las propiedades de los cueros resultantes fueron analizadas cualitativamente y cuantitativamente, y los estudios de SEM se llevaron a cabo para las pieles tratadas. Este trabajo proporciona una base para el desarrollo de mejores agentes engrasantes.

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INTRODUCTION

Surfactants are able to modify the interfacial[1] properties of a system by changing the surface tension. It is the amphiphilic[2] nature of surfactant molecules that makes them bifunctional. In recent years, accompanied by the progress of society and the development of surface science and technology, the application fields of surfactants have expanded. Sulfosuccinate type anionic surfactants are surface active metal salts of either monoester or diester of sulfosuccinic acid.[3] These are obtained by reacting maleic acid anhydride with hydroxyl groups carrying molecules, followed by sulfonation of the intermediate product, an ester. Chemistry of bisulfite addition to ethylenic double bonds is well documented[4] in the literature. The bisulfite addition to mono- and di-alkyl esters of maleic acid is a common method to produce corresponding sulfonate derivatives. These surfactants are of great interest because of their foaming, strong wetting, emulsifying, solubilising properties, extraordinary surface activity, high effectiveness in reducing surface tension, biodegradability, great mildness and low critical micelle concentration. They have better usage as a surfactant in the manufacture of fatliquors which plays a crucial role on the properties of finished leather.

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 emusification power, zeta potential, surface tension and particle size. 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.

EXPERIMENTAL

Materials and Methods

Materials

Lauryl maleate monoester (LAME) (Acid value: 160, pH: 6.0) used for the study. Other chemicals like sodium bisulfite, tetrabutyl ammonium bromide and isopropyl alcohol were used as AR grade without any further purification. Lauryl alcohol, 8 moles of ethoxylate, was industrial grade product.

Control batch

LAME (284g) was sulfonated using 120g sodium bisulfite dissolved in 480g water. Reactants were maintained at 70-75ºC for 3h.

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 70-75ºC for 3h.

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 70-75ºC for 3h.

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 70-75ºC for 3h.

Application on Leather

Fatliquors were prepared as a formulation comprising 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 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.

Characterisation Methods

%SO_3 content[5] was determined as a volumetric cationic titration against standard hyamine (benzothionium chloride), using methylene blue as the indicator. Emulsification power[6] was determined as the separation time measurement. Zeta potential was measured using Zetasizer 2000, model DTS 5202, of M/s Malvern Instruments Limited, UK. Surface tension was measured using KRUSS tensiometer K100 (KRUSS GmbH, Hamburg) at ambient temperature by ring balance method.[7] Particle size was measured using spectrex laser particle counter, (PC-2200^R), size range 1-100 microns.

The properties of resultant leathers were measured qualitatively and quantitatively. Scanning electron micrographs of the dried leather samples were taken using JEOL 400 microscope after spin coated with gold. Softness, whiteness and surface touch of the treated resultant leathers were measured as an organoleptic property, by three different qualified leather technologists and reported as an average value. It was visually examined and measurements were given in the scale with a rating of 0-5. Tensile strength was measured using PROLIFIC tensile strength machine and grain crack strength was measured through PROLIFIC elastometer.

RESULTS AND DISCUSSION

%$SO_{3,}$ Surface tension, Emulsification Power, Zeta Potential, Particle Size of all the prepared sulfosuccinates were shown in Table I.

TABLE I
Properties of sulfosuccinates.

Batch	% SO_3 (on 100% basis)	Surface tension (0.05% solution) (mN/M)	Emulsification power of 1% soln. (Time in sec)		Zeta Potential (mv)	Particle Size (Microns)		
			10ml	20ml		Min	Max	Mean
Control	5.2	32.92	40	87	-83.5	11	57	19.8
E1	6.9	32.11	45	100	-93.8	22	87	42.4
E2	11.3	29.05	70	147	-100.1	10	82	39.8
E3	14.6	31.16	60	139	-111.6	37	99.9	59.1

The particle size distribution analysis of all the sulfosuccinates were given in the Figure 1.

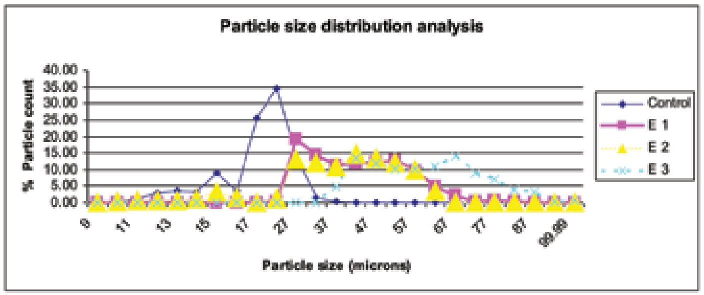

Figure 1. Particle size distribution of sulfosuccinates.

TABLE II
Properties of resultant leathers.

	Wet blue cow	
Parameter	**FL Control**	**FL E3**
Softness	4.5	5.0
Whiteness	4.5	5.0
Surface touch	4.5	5.0
Tensile strength (Kgs/Sqcm)	296	358
% Elongation	89	83
Grain crack strength (Kgs/cm)	344	380
Distension mm	12	12

Properties of Resultant Leather

The properties of resultant leathers such as softness, whiteness, surface touch, tensile strength and grain crack strength were shown in Table II.

SEM Studies

The scanning electron micrographs of dried leather samples were shown in Figures 2 and 3.

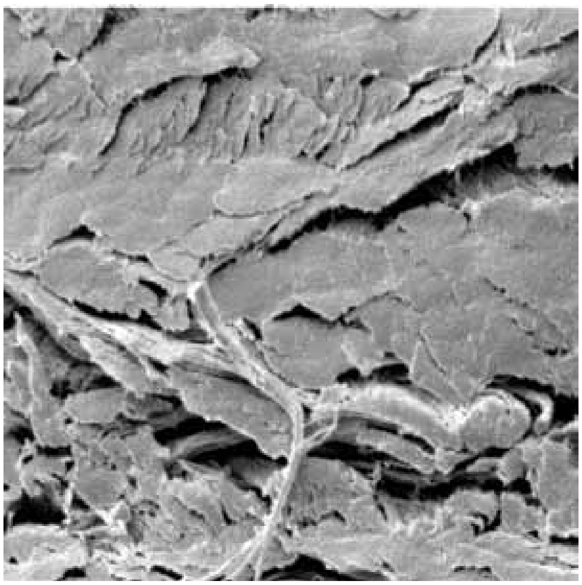

Figure 2. SEM photomicrograph of FL control at a magnification of 300 x.

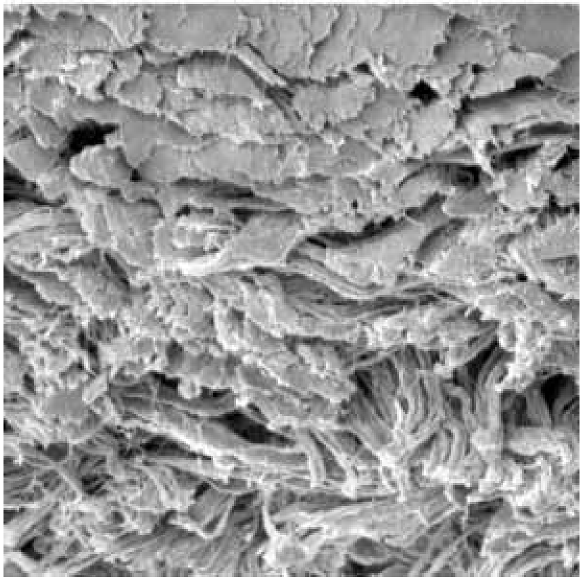

Figure 3. SEM photomicrograph of FL E3 at a magnification of 300 x.

Discussion

Sulfonate Content of the Surfactants

Sulfonate content of the sulfosuccinate plays an important role in deciding the surface activity. It is a crucial factor for the performance of a fatliquor on leather. Reaction efficiency will be indicated by the sulfonate content. It improves the leather properties softness, whiteness and surface touch. The major concern is about achieving maximum possible improvement in leather properties for industrial applications. Most of the results appears that the reaction conversion was self-limiting. A postulate for the self-limiting nature of the process is that sulfosuccination occurs via an interfacial process, whereby the ester has to migrate to the aqueous droplet interface. At the beginning of the sulfosuccination, sodium bisulfite added to 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 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 they 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 thought that the limiting conversion could be able to overcome by the addition of either phase transfer catalyst or non-ionic wetting agent or co-solvent. Accordingly, three experiments were performed and obtained the higher sulfonate contents. Table I showed that % Sulfonate content of the control batch was 5.2 and was increased by 1.33 times during the usage of phase transfer catalyst. This was further increased upto 2.17 times upon the usage of non ionic wetting agent and 2.80 times when co-solvent was used.

Effect of Co-solvent

Sulfosuccination is basically the result of two phase reaction in which the sulfonation occurs only in the ester phase. In the control batch, slow dissolving rate of the ester in the water medium caused the lower sulfonate content. Addition of isopropyl alcohol (IPA) as a co-solvent in E3 converted the reaction into a single phase process. IPA dissolves both reactants into one phase. In the single phase, the two reactants can physically contact with one another and are chemically reacting. The co-solvent increased the rate of reaction by making the ester soluble in the solvent and increasing the contact of the reactants.[8]

The formation of micelles takes place in the process due to the presence of IPA and reflected in terms of hydrophobic effect.[9-10] Addition of IPA in E3 produced marked changes in the critical micelle concentration (CMC). This is because of the tendency of IPA either to break or make the water structure through solvation[11] 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 associating with the molecules of the surfactant and therefore delaying the aggregation of the surfactant monomers to form micelles.

Additional effects results from hydrogen bonding ability of co-solvent,[12-19] the changes in the polarity and hydrophobicity 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[20] of the medium and thus decreased the dissociation of the surfactant monomers and micelles as well. The hydrophobic tail of the initially formed surfactant interacts with the hydrophobic part of the organic solvent and causes a shift of the surfactant molecules from the interface to the bulk of the solution. This resulted in higher reaction rate and conversion, yielded the maximum sulfonate content as observed in Table I.

Effect of Emulsifier

The added non-ionic emulsifier, lauryl alcohol-8 moles of ethoxylate (LA8EO) in E2 physically surround one reactant and transport to the other reactant. This allowed the physical contact and hence chemical reaction of two reactants. LA8EO reduces the viscosity of the surrounding system and also provides the homogeneity of the medium. This provides better control of the reaction to attain more degree of sulfonation as achieved in E2. Emulsifier have a lipophilic and a hydrophilic poles. The lipophilic part bonds with the ester and the hydrophilic part bonds with the water thereby facilitates the faster reaction rate. They 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. The reaction rate and the conversion were very slow as depicted in the case of control batch. Addition of LA8EO in E2 lead to micellar catalysis[21] where the lipophilic reactants were solubilised in the emulsifier micelles. The swelled micelles disperse in water phase containing hydrophilic reactants. The reaction interface area between oil phase reactants and water phase reactants was enlarged greatly. The interface magnifying effect, electrostatic interaction and concentrating effect result in dramatic increase in the reaction rates.[22-23]

Above CMC, the number of micelles increased with the addition of emulsifier which resulted in fast reaction and a higher conversion. Further increase of addition of LA8EO induced micelles to expand, which in turn cause slow increase of oil/water interfacial area. It results in gradual 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 same can make reaction conditions gentle and effectively inhibit side reactions to occur. And it will enhance the efficiency of the reaction.

Effect of Phase Transfer Catalyst

Addition of tetrabutylammonium bromide[24] (TBAB) in E1 was found to be versatile synthetic technique applied to intensify the slow heterogeneous reactions of liquid-liquid or liquid-solid reactants.[25] It decreases the reaction activation energy, accelerate reaction speed by making conditions convenient and inhibit side reactions.[26-28] All these factors increased the sulfonate content of sulfosuccinates. The primary function of TBAB is to move an ion in a reactive state from one phase to a second phase. It performs a true catalytic function by first disassociating from its anion and associating with a different anion in the first phase. It carries the anion in a reactive state across the phase boundaries between the first and the second phases. The ion reacts with a constituent in the second phase. The catalyst now reassociates with the anion and returns to the first phase in its original form to catalyze another phase transfer. It promotes ion pair formation and simultaneously disturbs mass transfer across the interface.

In the phase transfer catalysis, addition of anion supplied as metal salt - sodium bisulfite in E1 and was transferred gradually from the aqueous phase into the organic phase by the intervention of an onium[29] salt. The sulfite was extracted as in onium salt into the organic phase. The onium sulfite reacted with the double bond of the ester to form sulfosuccinate. The reaction conditions 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 so that chemical reaction happens. Following the reaction of 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[30] to dissolve both aqueous and organic liquids. There were several advantages of being employed as phase transfer catalysis in the industrial processes such as an increased reaction rate, mild reaction temperature and pressure, avoiding the employment of expensive anhydrous or aprotic solvents.

Properties of Sulfosuccinates

Surfactant properties such as surface tension, emulsification power and zeta potential (Table I) showed that the measurements were in accordance and direct agreement with the surfactant activity of the sulfosuccinates. The 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. In E2, there was an addition in surfactant activity due to the added emulsifier also. Hence, slight further marginal reduction upto 29.05 mN/m in E2.

Emulsification power showed a positive variation with respect of 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. There was a slight variation observed in the case of E2, where external emulsifier was added. The observed values were 70 and 147 seconds. The values for E3 were 60 and 139 seconds respectively. Emulsification power was the capacity of the surfactant to bind the neutral oil present in the system. In the control, E1 and E3, emulsification power was only due to the sulfosuccinate component whereas, in the case of E2, there was a combination from sulfosuccinate and the added external emulsifier. Hence, E2 values were higher than E3, eventhough it had slightly lower sulfonate content than E3.

In the case of zeta potential, there was an increase in trend observed with the increase in the sulfonate content. Zeta potential values of the control batch, E1, E2 and E3 were -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 stability increased and showed positive increase trend of zeta potential. Higher zeta potential provides better stability, which is an important factor in the fatliquor systems.

The particle size measurements (Table I) showed that there was not much variation between the sulfosuccinates of different sulfonate contents. 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 sulfonation was not found to be linear as expected. It showed negative trend in E2 whereas positive trend in E1 and E3. Instead of sulfonate content, the added additives like TBAB, LA8EO and IPA played the role in deciding the particle size of the surfactants.

Properties of Resultant Leathers

The performance of fatliquors prepared from the control batch and E3 batch were compared. E3 batch showed very clearly the better performance of fatliquor in the properties of softness, whiteness and surface touch, each to the extent of 11%. Tensile strength and grain crack strength were improved by 21% and 11% respectively. The difference of higher degree of sulfonation of 2.8 times played the critical role in deciding the performance.

Higher surfactant activity changed the imparted leather parameters in the positive direction. The possible reason is that a lower content of emulsifier in a fatliquor results in neutral oil depositing[31] on the surface of the leather, resulting in lower performance. The other important criteria for the leather performance were 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 into the leather for good absorption.

The performance depends on the particle size also. When the particle distribution was homogeneous, 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 as indicated in Table I and Figure 1.

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

Grain pattern of dried leathers at a magnification of 300 x are given in Figures 2 and 3. The fibre splitting of the grain was very well observed in Figure 3. The fatliquoring composition having E3 surfactant facilitates the better penetration in leather. This resulted in better lubrication of fibres and reflected in their better performance in all aspects as compared to fatliquor having control batch surfactant.

CONCLUSIONS

During the sulfosuccination of the maleate monoester the addition of phase transfer catalyst, non-ionic wetting emulsifier and co-solvent were found to improve the degree of sulfonation by 33%, 117% and 180% respectively. Sulfonate content had a direct effect on emulsification power, zeta potential and surface tension, whereas the additives phase transfer catalyst, non-ionic wetting agent and co-solvent played a role in deciding the particle size. Fatliquors were prepared using sulfosuccinate having 5.2% and 14.6% sulfonate content and applied on wet blue full chrome leather. Leather properties were studied qualitatively and quantitatively. This was further confirmed by SEM studies. The fatliquor with the sulfosuccinate of 14.6% sulfonate content yielded a better leather performance in the aspects of softness, whiteness, surface touch, tensile strength and grain crack strength. Judging from the conditions employed, this study has great prospects for industrial applications.

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