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Interfacial properties of novel surfactants based on maleic and succinic acid for potential application in personal care



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ABSTRACT

Hemiesters and Hemiamides of maleic and succinic acid viz. sodium lauryl succinate (C12SE), sodium lauryl maleate ($C_{12}ME$), sodium lauryl succinamide ($C_{12}SA$), sodium lauryl maleamide ($C_{12}MA$), sodium hexadecyl succinate (C16SE) and sodium hexadecyl maleate (C16ME) were synthesized and investigated as surfactants in the pure water and aqueous hydrotrope [sodium *p*-toluene sulfonate (NaPTs)] solution. The chemical structures of the prepared surfactants were established by FTIR and ¹H NMR spectroscopy. The surface tension measurements depicted low CMC and a high adsorption efficiency (pC_{20}) which is highly beneficial for creating personal care formulations. The dynamic light scattering (DLS) technique indicated the formation of larger micelles which was important for skin care as larger micelles cannot penetrate the skin layer. Moreover, these surfactants depicted good foamability and stability attributed to faster monomer adsorption and small bubble size which was preferred for cleansing application. Additionally, low protein/lipid solubilization by these surfactants indicated its mild behaviour on skin as compared to other commonly used conventional anionic [sodium lauryl sulfate (SLS)], zwitterionic [cocamidopropyl betaine (CAPB)] and nonionic [decyl glucoside (DG)] surfactants. Viscosity measurements suggested decent thickening ability of surfactants in the presence of co-surfactant like lauramine oxide. Basis of all the properties discussed, these novel hemiesters and hemiamides seem promising as surfactants for improving various characteristics in potential personal care formulations.

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1. Introduction

The self-assembly of amphiphilic molecules show an imperative role in natural and industrial applications [1–5]. The driving force for self-assembly stems from the interplay between hydrophobic and hydrophilic interactions of the amphiphile. Depending on the molecular architecture and solution conditions (presence of salt, co-surfactant, temperature, etc.), surfactants form numerous aggregates of well-defined shapes and sizes beyond the critical micelle concentration [6–10]. Anionic surfactants have gained much consideration from the scientific community in the past few years and are expected to further increase owing to their unique physicochemical properties [11–15]. This compels the improvement of new anionic surfactants possessing a high surface activity, excellent adsorptive ability, and is mild to skin by judiciously tuning their molecular structure. Besides the continual task

of finding means to reduce the manufacturing cost for prevailing surfactants, appeal for 'greener' products is the dominant driving force for surfactants development.

Numerous different classes of surfactants can be synthesized from simple amino acid building blocks [16–18]. These surfactants have been comprehensively explored with respect to dermatological properties, surface activity and foaming properties and serves as a vital asset in personal care formulations. Hemiesters and hemiamides of maleic acid and succinic acid with different chain lengths (C_8 - C_{16}) of the hydrophobic alkyl group were synthesized by Abele et al. and were used as surfactants in the emulsion polymerization of styrene and butyl acrylate [19,20]. However, they did not report comprehensive interfacial properties of these surfactants owing to their low solubility in pure water. The succinates have an analogous structure to maleates, but they do not contain any reactive double bonds. Hence it would be interesting to explore their comprehensive surface properties.

In this context, we have synthesized hemiesters and hemiamides with lauryl chain length and hemiesters of maleic acid and succinic acid with hexadecyl chain length by adopting the method reported by Abele et al. [19] and finally neutralizing them



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with aqueous sodium bicarbonate solution. Physicochemical properties of these surfactants were explored for the first time which could be highly beneficial for their application in personal care formulations. These surfactants displayed intriguing interfacial properties but lower water solubility. However, we found that overall solubility of these surfactant could be increased in the existence of hydrotropes (sodium *p*-toluene sulfonate; NaPTs) which were structurally similar to surfactants (but possess a weaker hydrophobic character) and have many practical applications [21,22]. On the basis of various theoretical and experimental efforts, it is widely accepted that there is a formation of a complex between hydrotropes and additives, which would then show a higher aqueous solubility.

This paper will encompass fundamental information relating to synthesis, basic characteristics, and the physicochemical properties of novel surfactants based on maleic and succinic acid like sodium lauryl succinate ($C_{12}SE$), sodium lauryl maleate ($C_{12}ME$), sodium lauryl succinamide ($C_{12}SA$), sodium lauryl maleamide ($C_{12}MA$), sodium hexadecyl succinate ($C_{16}SE$) and sodium hexadecyl maleate ($C_{16}ME$) in pure water and aqueous NaPTs solution. The chemical structures of the prepared surfactants were established by FTIR and ¹H NMR spectroscopy. Measurements of critical micelle concentration (CMC) made by surface tension and size distribution of the micelles was derived using dynamic light scattering (DLS) techniques. In addition, the foaming behavior was investigated and the protein/lipid solubilization by surfactants was examined. Viscosity measurements were performed by using Brookfield viscometer.

2. Experimental section

2.1. Materials

Surfactants used in the study like sodium lauryl succinate, sodium lauryl maleate, sodium lauryl succinamide, sodium lauryl maleamide, sodium hexadecyl succinate and sodium hexadecyl maleate were synthesized (were pure as confirmed by NMR measurements in supporting information) in the laboratory. Sodium *p*-toluene sulfonate (>98%, Sigma), Zein protein (>98%, Sigma) and stearic acid (>98%, TCI) were used as received. All experiments were carried out using Milli-Q water. Samples were allowed to equilibrate for at least 24 h before measurement.

2.2. Methods

2.2.1. Surface tension

Surface tension of the various concentration of surfactant was determined using a Du Nouy tensiometer (Type: K20, KRÜSS, Germany) using a platinum plate method. Each experiment was conducted by using 20 mL of the sample in a 50 mL beaker. In this method, the liquid to be examined was taken in a vessel whose position can be changed by moving it up and down with the help of a screw. A platinum plate was positioned at the top of the vessel. During the process, distance between the liquid surface and immersed plate was kept approximately 3 mm to ensure the plate was just below the liquid surface. The pre-programmed software in the tensiometer measures the surface tension of the surfactant solutions. The tensiometer was calibrated using deionized Milli-O water and surface tension values $(71.8 \pm 0.1 \text{ mNm}^{-1})$ at $27 \pm 1 \degree \text{C}$ agreed well with the literature. After each reading, the plate was washed thoroughly by double distilled water and then heated in burner flame. The readings were taken in triplicate to ensure the reproducibility and accuracy of measurements.

Foaming Behavior: Foaming experiment was performed using a simple handshake method in 100 mL self-standing measuring

cylinder by vigorous shaking for 60 s. Sample taken in each cylinder was 10 mL; 0.3 wt%. The foamability was determined by noting the foam height immediately after shaking and images were taken at 27 ± 1 °C. Foam stability was determined by observing the change in foam height with respect to time. Foamability and foam stability were also evaluated using Ross Miles method [23] with these surfactants (250 mL; 10 mM). Initially column was rinsed with double distilled water, then walls of column was rinsed with surfactant solution till 50 mL surfactant solution was stored at bottom and remaining approximately 200 mL of surfactant solution was filled into a pipette. That pipette was immediately placed at top of column and the stopcock of pipette was slowly released. When all the solution had run out of the pipette, stopwatch was started to take readings of the foam height at initial time (foamability) and again reading of the foam height was recorded after 5 min which helps to determine the foam stability.

2.2.2. Protein solubilisation

Surfactants diminish the barrier properties of the skin proteins leading to their swelling and denaturation. The tendency of surfactants to interact with model proteins (e.g., Zein - one of the best understood plant protein) has been concomitant with their harshness toward human skin. Thus, higher the tendency of a surfactant to interact (higher the solubilization of Zein protein); higher is its inclination to irritate human skin. Protein (Zein) solubilization by as-synthesized surfactants was determined by gravimetric analysis. Surfactant solutions were taken in a vial and approximately 15 wt% Zein powder was added to it (excess of Zein). Now, the mixture of Surfactant-Zein was kept for continuous shaking for about 24 h. After that, the mixture of surfactant-Zein was filtered using Whatman filter paper. In the end, solid collected was dried at 80 °C for 24 h. From the weight of insoluble Zein after 24 h of drying, the wt% of solubility of the protein in surfactant was calculated. This experiment can clearly give us the amount of Zein protein solubilized by each surfactant at particular concentration. From this data we can compare the mildness property (harshness) of the surfactants for using them in personal care formulations.

2.2.3. Lipid solubilisation

Lipid (stearic acid) solubilization was determined by gravimetric analysis. Surfactant solutions were taken in a vial and approximately 1 wt% stearic acid powder was added to it (excess of stearic acid). Now, the mixture of surfactant-stearic acid was kept for continuous shaking for about 24 h. After that, the mixture of surfactant-stearic acid was filtered using Whatman filter paper. In the end, solid collected was dried at 60 °C for 24 h. From the weight of insoluble stearic acid after 24 h of drying, the wt% of solubility of the lipid in surfactant was calculated.

2.2.4. Viscosity measurements

Viscosity measurements were performed with Brookfield viscometer (DV 2T) with Spindle No. 15 for 1 min. Required amounts of samples in vials were homogenized and kept at 27 ± 1 °C for at least 24 h to ensure equilibration before performing viscosity measurements. Reproducibility (triplicate) was checked for the samples and no significant differences were observed.

2.2.5. Micellar size and zeta potential measurements

Micellar size and zeta potential was determined using Dynamic Light Scattering (Zetasizer Nano-ZS, ZEN3600) Malvern instruments Ltd. The surfactant solutions of different concentrations (1 mM, 5 mM and 10 mM) were taken directly into the quartz cell. The temperatures of the measurements were controlled around $27 \pm 1 \,^{\circ}$ C.

2.2.6. Microstructure of foams

At first, foam was generated by using the hand shaking method. Then the microstructure of foam bubbles was observed with the Olympus STM7CB Digital Microscope.

3. Results & discussion

3.1. Synthesis of novel surfactants

Synthesis of surfactants was started with maleic or succinic anhydride as starting materials. Opening of these cyclic anhydrides either with long chain alcohols or amines result in the formation of hemiesters or hemiamides [19,20]. Later, the carboxylic acid group was converted to respective sodium salts by treating with sodium bicarbonate to get required surfactants of interest. Synthesized surfactants were pure, as per the NMR recorded for the intermediates; hemiester carboxylic acids and hemiamide carboxylic acids. They were converted into corresponding carboxylates by using exactly one equivalent of sodium bicarbonate (NaHCO₃) to get a clean product without any unwanted side products or unreacted reactants and reagents. Also the melting point determination for intermediates; hemiester carboxylic acids and hemiamide carboxylic acids were in line with that reported by Abele et al [19]. The schematic representation of the synthesis of each surfactant was presented below, while the experimental details pertaining to synthetic procedures and analytical data of surfactants were designated in the supporting information.

3.2. Synthesis of sodium lauryl maleate: $(C_{12}ME)$



3.3. Synthesis of sodium lauryl succinate: $(C_{12}SE)$



3.4. Synthesis of sodium lauryl maleamide: $(C_{12}MA)$



3.5. Synthesis of sodium lauryl succinamide: (C₁₂SA)



3.6. Synthesis of sodium hexadecyl maleate: $(C_{16}ME)$



3.7. Synthesis of sodium hexadecyl succinate: $(C_{16}SE)$



4. Adsorption at the air-liquid interface

Surface tension (γ) measurements were executed to explore and estimate the surface active properties of as-synthesized surfactants in pure water. Longer alkyl chain surfactants were insoluble in water because of their high hydrophobicity. The equilibrium surface tension versus concentration plot obtained for sodium lauryl succinate ($C_{12}SE$) and sodium lauryl succinamide ($C_{12}SA$) were depicted in Fig. 1a, and for sodium lauryl maleate (C12ME) and sodium lauryl maleamide ($C_{12}MA$) was presented in Fig. 1b. The measured surface tension isotherms for different concentrations do show a characteristic decline in surface tension with increase in surfactant concentrations and then reaches a plateau region, beyond which a practically constant value for surface tension is observed. The critical micelle concentration (CMC) values for each of these surfactants were acquired by analyzing the intersection point of the plots. Two essential factors, the efficacy of surface tension decrease (π_{CMC}) and the adsorption competence (pC_{20}), can also be inferred from the measured surface tension data using the following Equations (1) and (2) respectively [24]. Typical structures, CMC values, $\pi_{\rm CMC}$ and pC_{20} for all the individual surfactants were listed in Table 1.

$$\pi_{\rm CMC} = \gamma_0 - \gamma_{\rm CMC} \tag{1}$$

$$pC_{20} = -\log C_{20} \tag{2}$$

where γ_0 and γ_{CMC} was the surface tension of pure water and surface tension of surfactant solution at CMC. While C_{20} was the concentration of surfactant required to reduce the surface tension of water (i.e. 71.8 mN/m) by 20.0 mN/m.

It can be concluded from Table 1 as well as Fig. 1a and 1b that CMC values of these surfactants were in accordance with the structural characteristics, i.e., $C_{12}SE$ and $C_{12}ME$ display slower adsorption rate (less surface active) at the surface and higher CMC values compared to $C_{12}SA$ and $C_{12}MA$ with identical hydrocarbon chain length respectively. The presence of amide group in $C_{12}SA$ and $C_{12}MA$ attributes to lower CMC as it was prone to H-bonding [25]. The solubility of surfactants in water was basically directed



Fig. 1. Equilibrium surface tension versus concentration curve in pure water of (a) $C_{12}SE$, $C_{12}SA$ (b) $C_{12}ME$, $C_{12}MA$ and (c) $C_{12}SE$ (d) $C_{12}ME$ in pure water and 1 wt% NaPTs solution.

by the balance amongst the hydrophobic and hydrophilic groups and also on the ability of the molecules to pack into organized structures. Sodium hexadecyl succinate ($C_{16}SE$) and sodium hexadecyl maleate ($C_{16}ME$) with longer hydrocarbon chains were almost insoluble in aqueous medium and hence the CMC values were not reported here.

We have observed that solubility of $C_{16}SE$ and $C_{16}ME$ (which is practically insoluble in pure water) could be enhanced in the presence of small amount (1 wt%) of hydrotropes such as sodium *p*toluene sulfonate (NaPTs). We had tried several hydrotropes like NaS, Sodium salicylate; NaPTs, Sodium p-toluene sulphonate; and NaXS, Sodium xylene sulphonate. However we found that NaPTs worked well and also it is widely utilized in personal care formulations. This allows to explore the interfacial behavior of $C_{16}SE$ and $C_{16}ME$ in NaPTs solution at room temperature and their CMC values are listed in Table 1. Fig. 1c and d show the surface tension curves for $C_{12}SE$ and $C_{12}ME$ solutions in the absence and presence of NaPTs. Since the hydrotropes are themselves weakly surface active were capable of cooperatively forming aggregates in the presence of other surfactants. The CMC values of $C_{12}ME$ and $C_{16}ME$ agrees well with the reported data [19].

As indicated in Fig. 1c and d, presence of NaPTs considerably lower the surface tension of $C_{12}SE$ and $C_{12}ME$ signifying increased surface activity of the mixed system owing to favorable interactions and allowing the micelle formation at much lower concentration (decrease in CMC) as compared to pure water. However, there was no appreciable change in the final limiting value of the surface tension. Furthermore smaller value of pC_{20} for $C_{12}SA$ and $C_{12}MA$ indicates that it can more competently adsorbed at the interface and decreases surface tension. The CMC values obtained for all the surfactants in the presence and absence of NaPTs obtained from the distinct break in the surface tension–log concentration

Table 1

Critical micelle concentration (CMC) of surfactants in pure water and 1 wt% NaPTs at 27 °C. * indicates CMC values from Ref. [19].

Surfactant	Structure	CMC, mM		Усмс	p <i>C</i> ₂₀	$\pi_{\rm CMC}$
		Water	NaPTs	NaPTs		
Sodium lauryl succinate (C ₁₂ SE)	O ONa O O	0.50	0.40	27.3	0.022	44.7
Sodium lauryl maleate (C ₁₂ ME)	ONa	0.40	0.27 (0.32)*	28.1	0.018	43.9
Sodium lauryl succinamide (C ₁₂ SA)	0 ONa	0.15	0.14	38	0.014	34
Sodium lauryl maleamide (C ₁₂ MA)	ONa NH C ₁₂ H ₂₅	0.37	0.27	29	0.016	43
Sodium hexadecyl succinate (C ₁₆ SE)	ONA	Insoluble	0.14	32.2	0.024	39.8
Sodium hexadecyl maleate (C ₁₆ ME)	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Insoluble	0.22 (0.23)*	30.9	0.014	41.1
	O C ₁₆ H ₃₃					

plots were also recorded in Table 1. Additionally, we have also observed that use of potassium or organic counterions such as Triethanolamine (TEA) can also increase the overall solubility of synthesized surfactants to some extent (data not shown).

5. Micellar size and charge

Micellar size and micellar charge was evaluated for each surfactant based on dynamic light scattering (DLS) and zeta potential measurements at CMC in pure water and NaPTs solution (1 wt%). The obtained results were reported in Table 2. We have also included widely utilized conventional surfactants in personal care like anionic sodium lauryl sulfate (SLS), zwitterionic cocamidopropyl betaine (CAPB) and nonionic decyl glucoside (DG) for comparison.

The results from DLS clearly indicates that micellar size of synthesized surfactants was much larger both in pure water and in the presence of aqueous NaPTs which could be attributed to the formation of some kind of aggregated structure. However, micellar sizes of SLS, CAPB and DG was much smaller than synthesized surfactants measured at CMC. This clearly indicates different aggregation behavior of synthesized surfactants compared to conventional surfactants. Furthermore, $C_{12}SE$ and $C_{12}ME$ displays bigger micellar size and micellar charge at similar concentrations compared to same hydrocarbon chain length $C_{12}SA$ and $C_{12}MA$ respectively. Bigger micelles were preferred for skin care formulations as they cannot penetrate the skin easily.

6. Foaming behavior

Foam creating power of the liquid or foamability was referred to the capability of the surfactants to accomplish low surface tension in a short time when a fresh interface was created. The foam stability of a surfactant solution was defined as the alteration in foam volume which was primarily controlled by the drain speed and intensity of the interfacial film. Foam construction and permanency were imperative in numerous applications [26–28]. The surfactant molecules adsorb to the air/water frontier, allowing the formation of stable foams. While low surface tension was more advantageous for foam creation, several factors play decisive role in the stability of aqueous foams once it is created, for e.g., interfacial tension, bubble size, film rigidity and drainage.

Fig. 2(a) depicts representative plot for foaming behavior observed by Ross Miles method for each surfactant (10 mM; 250 mL) in the presence of 1 wt% NaPTs. Foaming behavior of all the surfactants shown in Fig. 2 was studied in the presence of NaPTs since $C_{16}SE$ and $C_{16}ME$ were practically insoluble in pure water it and would not be possible to study their foaming behavior in water. All the studied surfactants exhibited good foaming capacity within the tested concentration range. However, relatively speaking, the foamability of lauryl chain surfactant $C_{12}SE$, $C_{12}SA$, $C_{12}ME$ and $C_{16}ME$. The average foaming volumes (foam height) and half-lives of each surfactant exceed 150 mL and 30 min, respectively, at a defined concentration. It has also been inferred from surface tension measurements that each of these surfactants have the ability to lower surface tension of water to as low as 30 mN/m

Table 2

Micellar size and zeta potential for surfactants determined at CMG	C in pure water and NaPTs solution at 27 °C.
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Surfactant	Water	Water		NaPTs		
	Size (nm)	Zeta potential (mv)	Size (nm)	Zeta potential (mv)		
C ₁₂ SE	105	-45.6	109.3	-50.3		
C ₁₂ ME	127.5	-60.4	130.1	-63.6		
C ₁₂ SA	67.6	-13.2	72.1	-20.1		
C ₁₂ MA	32.6	-36.1	37.2	-40.3		
C ₁₆ SE	-	-	75.6	-60.2		
C ₁₆ ME	-	-	98.2	-66.4		
SLS	9.6	-57.6	11.6	-61.4		
CAPB	15.8	-1.4	17.8	-3.4		
DG	19.4	-19.5	22.1	-21.8		



Fig. 2. (a) shows the plot of foam height of each surfactant (10 mM) and (b) shows the representative photograph of foaming behaviour C₁₂SE in the presence of 1 wt% NaPTs at 27 °C.



Fig. 3. Optical microscopy images of foam generated from 10 mM surfactants solution (a) $C_{12}SE$, (b) SLS, (c) CAPB and (d) DG in the presence of 1 wt% NaPTs solution at 27 °C. Inset shows the photo of the foam for the corresponding surfactants.

which in turn can be good at stabilizing the initial foam created during the lathering phase. The foam once created also stays intact for few hours depicting the reasonable foam stability required for many applications. The foamability and foam stability measurements from the Ross Miles methods were also supported by hand shaking methods shown in photo in Fig. 2(**b**) for $C_{12}SE$.

We had also generated foams using solution (10 mM) of surfactant $C_{12}SE$, SLS, CAPB and DG in 1 wt% NaPTs and observed under the microscope to understand the bubble size and foam structures as depicted in Fig. 3. Foam generated from SLS and CAPB contained higher liquid fraction and large bubble sizes. While DG and $C_{12}SE$ produces foam with low liquid fraction and much smaller bubble sizes. This observations indicate that synthesized surfactants could serve as a good foaming agents for several applications.

7. Viscosity measurements

Measurement of the rheological properties is one of the dominant tools to characterize the properties of different surfactant



Fig. 4. Viscosity measurements performed for various surfactants (5 wt%) in the presence of lauramine oxide (as active %) at 27 °C and pH 5.5. Dash line was only for pure lauramine oxide without any other surfactant. Inset photo showed the micellar transition from sphere-rod as indicated by trapping of the air bubbles for $C_{12}SE$.

solutions, which in many cases are non-Newtonian. Viscoelastic properties have been reported in anionic and mixed-surfactant systems comprising of cationic–anionic and anionic–zwitterionic surfactants [29,30]. Because of the electrostatic interactions between anionic surfactant headgroups, the growth of micelles in the solution is inadequate. But with inclusion of salts, cosurfactants or other additives to the solution, electrostatic repulsive forces in an ionic micelle are reduced, thus promoting micelle growth. We have studied the viscosity behavior for $C_{12}SE$ and $C_{12}ME$ in the presence of lauramine oxide. Also, we have used SLS and DG for comparison under similar conditions.

Fig. 4 illustrates the plot of viscosity of surfactants like $C_{12}SE$, $C_{12}ME$, SLS, and DG in the presence of varying concentrations (as active %) of lauramine oxide (LAO) which is an amine oxide based nonionic surfactant, with a C_{12} (dodecyl) alkyl tail. Lauramine oxide is a common co-surfactant used often as foam booster in consumer products. Pure lauramine oxide showed negligible change in viscosity with concentration as indicated by dash line.

We have found that $C_{12}SE$ or $C_{12}ME$ solution (5 wt%) in the presence of lauramine oxide at pH 5.5 could result in formation of long flexible micelles imparting high viscosity to the sample. This can be explained by assuming that the repulsion between the charged anionics C₁₂SE or C₁₂ME is shielded by the presence of the lauramine oxide in the mixed micelle. We adjusted the pH to 5.5 (by using citric acid) to achieve the desired viscosity for that particular binary surfactant composition as lauramine oxide being zwitterionic exhibits variation with change in pH. Moreover, Fig. 4 also reflects that SLS shows slightly higher viscosity than assynthesized surfactants, while DG shows almost negligible viscosity change in the presence of lauramine oxide. Viscosity results for as-synthesized surfactants clearly specify their good prospective with decent thickening ability in the presence of the cosurfactant like lauramine oxide. It can be seen from Figure that C12SE and C12ME exhibit moderate viscosity build-up with LAO performing better than non-ionics though not as good as SLS.

In C_{12} SE-lauramine oxide or C_{12} ME-lauramine oxide mixtures at lower total surfactant concentration (below 8 wt%) the viscosity remains low. While, sphere-to-rod micellar transition was observed in both C₁₂SE and C₁₂ME at higher surfactant concentration in the presence of lauramine oxide as evidenced by the inset photo in Fig. 4 which depicts the air bubbles trapped in the viscous solution. This brings about a sharp increase in the solution viscosity (>500 cP) attributed to the ability of lauramine oxide to reduce the average cross sectional area of the $C_{12}SE$ or $C_{12}ME$ and SLS therefore induce one-dimensional micellar growth leading to the formation of the elongated micelles. The addition of lauramine oxide to C12SE or C12ME also causes an escalation in the bulk viscosity by enhancing the packing at the air-liquid interface. At rest, the micelles were arranged randomly, which leads to a very high viscosity and clear solution as shown in inset photo. With increasing shear, the micelles get oriented parallel - and hence the viscosity decreases. This process was reversible: with decreasing shear, the micelles were arranged randomly again - the viscosity increases. The entire viscosity spectrum represented in figure gives us very clear understanding of the variation in viscosity with surfactants content. This helps us to choose the content of mixed surfactants with anticipated viscosity range for designing the formulations.

8. Skin mildness of surfactants

Stratum corneum (SC), the uppermost cover of the epidermis, affords a vital barrier function in intact skin. Surfactants reduce the barrier properties of the SC proteins leading to their swelling and denaturation, though the molecular mechanisms involved



Fig. 5. Plot displaying protein and lipid dissolution by various surfactants (0.3 wt%) at 27 $^\circ\text{C}.$

have not yet been entirely revealed [31]. The propensity of surfactants to interact with model proteins has also been associated with their severity toward human skin. Thus, higher the tendency of a surfactant to interact; higher was its inclination to irritate human skin. We have performed the dissolution study of Zein protein and stearic acid as representative for protein and lipid by assynthesized surfactants (0.3 wt%) and the results are presented in Fig. 5. We have also made comparisons with standard sodium lauryl sulphate (SLS) which is known to interact strongly with Zein protein and was considered as very harsh to the skin [32]. As can be seen, the tendency of as-synthesized surfactants to dissolve Zein protein and stearic acid was very low (0.15–0.18 wt%) as compared to SLS (0.7 wt%) indicating "mildness" of these surfactants w.r.t topical/ skin cleansing applications.

It was believed that protein denaturation was basically owing to enormous compliant binding of surfactants and the subsequent escalation in the charge of the protein. Moreover, Blankschtein et al. [33] have established that micelle size is a main aspect in surfactant prompted irritation. Larger the micelle sizes, infiltration of the surfactant into deeper layers declines and so growing the micelle size was a tactic to augmenting mildness. In principle, the micellar size measured by DLS for each surfactants ($C_{12}SE$, C₁₂SA, C₁₂ME, and C₁₂MA) shown in Fig. 2 is relatively large and consequently have the potential to ease swelling and ability to reduce consequent penetration under cleansing conditions. Additionally, the in-built propensity of the molecule to cause an irritation response may also be allied to the charge density of the molecule [33]. However, we can say that all the as-synthesized surfactants shows mildness towards both protein and lipids compared to SLS, which can be attributed to its larger head group area and lower micellar charge.

9. Conclusions

Synthesis and physicochemical properties of novel surfactants based on maleic and succinic acid like sodium lauryl succinate, sodium lauryl maleate, sodium lauryl succinamide, sodium lauryl maleamide, sodium hexadecyl succinate and sodium hexadecyl maleate has been described. The chemical structures of these surfactants were established by FTIR and ¹H NMR spectroscopy. We have shown that solubility of these surfactants could be improved in the presence of hydrotrope like NaPTs. It was also demonstrated that the all synthesized novel surfactants display good surface activity and foaming ability. Moreover, they depict a tendency to get thicken with amine-oxides as co-surfactants and also exhibited 'mildness' with respect to skin, a property desired for use in topical preparations. Taken together, these surfactants had many of the characteristics that were desirable for industrial cleansing applications and hence was probable that this class of surfactants may in future become a part of formulators' tool-kit.

CRediT authorship contribution statement

Devi Sirisha Janni: Conceptualization, Methodology. **Gajendra Rajput:** Visualization, Investigation. **Niki Pandya:** Data curation. **Gayathri Subramanyam:** Supervision, Project administration. **Dharmesh Varade:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.117484.

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