Original Article

Thai Journal of Pharmaceutical Sciences

Synthesis of (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan – An amino sugar anionic surfactant under microwave irradiation and its application

P. S. Singh[1], Suraj N. Mali[2], N. R. Sangale[1], Amit P. Pratap[1]

[1]Department of Oils, Oleochemicals and Surfactants Technology (University Under Section-3 of UGC ACT 1956; Formerly UDCT/UICT; NBA Accredited "A" Grade by MHRD), Nathalal Parekh Road, Matunga (East), Mumbai, India, [2]Department of Pharmaceutical Sciences and Technology, Institute of Chemical Technology, (University Under Section-3 of UGC ACT 1956; Formerly UDCT/UICT; NBA Accredited "A" Grade by MHRD), Nathalal Parekh Road, Matunga (East), Mumbai, India

Corresponding Author:
Dr. Amit P. Pratap, Department of Oils, Oleochemicals and Surfactants Technology, Institute of Chemical Technology (University Under Section-3 of UGC ACT 1956; Formerly UDCT/UICT; NBA Accredited "A" Grade by MHRD), Nathalal Parekh Road, Matunga (East), Mumbai - 400 019, Maharashtra, India. Tel.: +91-22-3361 1111 2557. E-mail: ap.pratap@ictmumbai.edu.in

Received: Mar 16, 2021
Accepted: Jul 13, 2021
Published: Oct 13, 2021

ABSTRACT

Introduction: Chitosan, a biopolymer with 97% degree of deacetylation, was used herein, to synthesize an amino sugar anionic surfactant of varied alkyl chain length, using a microwave-assisted synthesis. We were also examined their properties in aqueous form. **Objectives:** The objectives of the study were to increase the surface activity and water solubility of chitosan derivatives. **Materials and Methods:** Structural features and crystallinity were confirmed using Fourier transform infrared, ^{1}H-nuclear magnetic resonance, and X-ray diffraction. The chitosan by itself was found to have weak surface-active properties since it has no hydrophobic segment. **Results**: The microwave-assisted synthesized sugar amino-based anionic surfactant, synthesis of (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan-succinyl chitosan was found to have excellent surface-active and detergency properties. The aggregation behavior of amino sugar anionic surfactant was characterized by surface tension, which indicated that it had good surface activity. **Conclusion:** We believe that good surface activities of synthesized water-soluble surfactants can be used in the formulations of face wash, body wash, liquid detergents, more applications in pharmaceutical, medicine and food industry, etc.

Keywords: Biologically extracted chitosan, Microwave irradiation, Chitosan-soluble derivatives, ^{1}H-Nuclear magnetic resonance, Chitosan, Anionic surfactants

INTRODUCTION

Chitin is a substance that is abundantly present in the exoskeleton of insects, crustaceans, and from other sources such as fungi, mushrooms, worms, and diatoms.[1,2] Chitin was found to be the second abundant natural polymer in nature after cellulose.[1,2] Chitin and its chitosan, a linear polysaccharide derivative, has several applications, such as emulsion stabilizers, rheology modifiers (particularly thickening agents), and in paints, oil recovery, cosmetic or foods industries, biomedical, food, emulsifying agent, wastewater treatment, biocatalysts, textile, paper industry, and agriculture.[3-8] Chitin can be extracted by means of either biological or chemical method (use of chemicals, as deproteinization reagents including NaOH, Na_2CO_3, $NaHCO_3$, and Na_2S), of which biological method has added advantage of environmentally benign approach.[9] Chitin isolation from shellfish requires the removal of the two major constituents of the shell, proteins by deproteinization and inorganic calcium carbonate by demineralization, together with small amounts of pigments and lipids that are generally removed during the two previous steps.[10] In some cases, an additional step of decolorization is applied to remove residual pigments. Many methods have been proposed and used over the years to prepare pure chitin; however, no standard method has been adopted. Both deproteinization and demineralization could be carried out using chemical or enzymatic treatments.

Chitin and chitosan are the homo-polysaccharides.[11] Chitosan is derived from *N*-alkaline deacetylation of chitin. Chitosan is amino glucopyrans composed of N-acetyl glucosamine and glucosamine (GlcN) residues with β-1,4 linkages.[11] A high-molecular-weight chitosan is having a very viscous nature; hence, it is less soluble.[11] Therefore, depolymerization of chitosan gives low-molecular-weight chitosan, which is less viscous and more soluble.[12-14] These polymers have specific functions due to their biological activity, biocompatibility, and complete biodegradability.

Chitosan biopolymer is available as an easily accessible reagent, because of its less crystalline nature than chitin.[12-14] After heating, chitosan decomposes before melting; therefore, it has no melting point.[12-14] The depolymerized chitosan has good solubility in dilute aqueous, organic, or mineral acids below pH 6.5.[15] To increase the solubility of chitosan, lots of efforts have been reported to synthesize functional derivatives by chemical modifications.

Surfactants are ubiquitously used in day-to-day life such as in medicines, cosmetics, soaps and detergents, and other household items.[16-18] They are used to decrease the surface tension between two liquids. By adding minute quantity of surfactant, changes in surface and interfacial properties of system can be observed. They tend to produce wetting, emulsifying, foaming, and dissolving characteristics. Out of four types of surfactants, cationic surfactants are used in hair shampoos, hair conditioners, and also in hard surface cleansers.[16-18] However, the performance of cationic surfactants is worse than that of anionic surfactants due to the higher percentage of non-polar portion,[19] which is difficult for their packing at molecular level.

Cationic surfactants are usually phytotoxic.[20] Non-ionic surfactants are usually used with another type of surfactants. As they are incapable to properly stabilize the air system created by them, they tend to lead coalescence and bubble coarsening. Thus, they are not frequently used as a single component. Like non-ionic surfactant, amphoteric surfactants are also less widely used, while anionic surfactants are most commonly used surfactants.[21] Anionic surfactants are the oldest development, the largest production, and the widest species in various types of surfactants. Anionic surfactants are used to remove clay, dirt, and some oily stains. Due to this property, they are the main component in detergents. A molecule of anionic surfactant is composed of a hydrophilic water-soluble "head" (such as SO_3-) and a lipophilic oil-soluble "tail" (typically an organic molecule C_{12}-C_{14}). Because of the excellent foam and lather characteristics of anionic surfactant, they are used in face wash, body wash, detergents, soaps, etc.[22]

Microwave synthesis represents a major breakthrough in synthetic chemistry for its excellent yield and low reaction time.[23-28] It can be seen that with the aid of the high-performance microwave reactor, one can achieve volumetric and selective heating, extremely rapid heat transfer, speed of switching on and off, pollution-free environment, and compactness of equipment as there are no products of combustion.[23-28] There are several reports available, who depict the advantage of microwave irradiation for chitosan modifications but very few papers compare these two techniques.[23-28]

Amino sugar anionic surfactant synthesized from chitosan by microwave synthesis would possess good surface active, detergency properties and act as excellent emulsifying agent. Surfactant molecules obtained from renewable source and raw materials which have natural lipoamino acids are best preferred choice for cosmetic and pharmaceutical application. They are biodegradable and non-toxic because of their simple and natural structures.[29] They can be easily synthesized using chemicals or by adopting an enzymatic route using raw materials such as vegetable oils and amino acid. Amphiphilic structure molecules with a high surface activity can be produced by the combination of amino acids or peptides as a hydrophilic part and the long-chain compounds as a hydrophobic part.

The current work presents the microwave-assisted synthesis of sugar amino acid-based anionic surfactants from the biologically extracted chitosan with 97% degree of deacetylation (DAD) [Figure 1]. As one of the water-soluble derivatives of chitosan, succinyl chitosan (SCCHS) has favorable properties as a drug carrier such as biocompatibility, low toxicity, and long-term retention in the body.[30] The free amino and hydroxy groups of SCCHS can act as useful intermediate, which permits other chemical modifications. Thus, based on a very recent study,[30] we thought worthwhile to modify the SCCHS by reacting chitosan with succinic anhydride under microwave irradiation, which was further treated with butyl glycidyl ether (BGE) to synthesize (2-hydroxyl-3-butoxyl) propyl-SCCHS (HBP-SCCHS) [Figures 1-8 and Tables 1-3]. The structure of the anionic surfactant was analyzed using Fourier-transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR), and X-ray diffractometer (XRD).

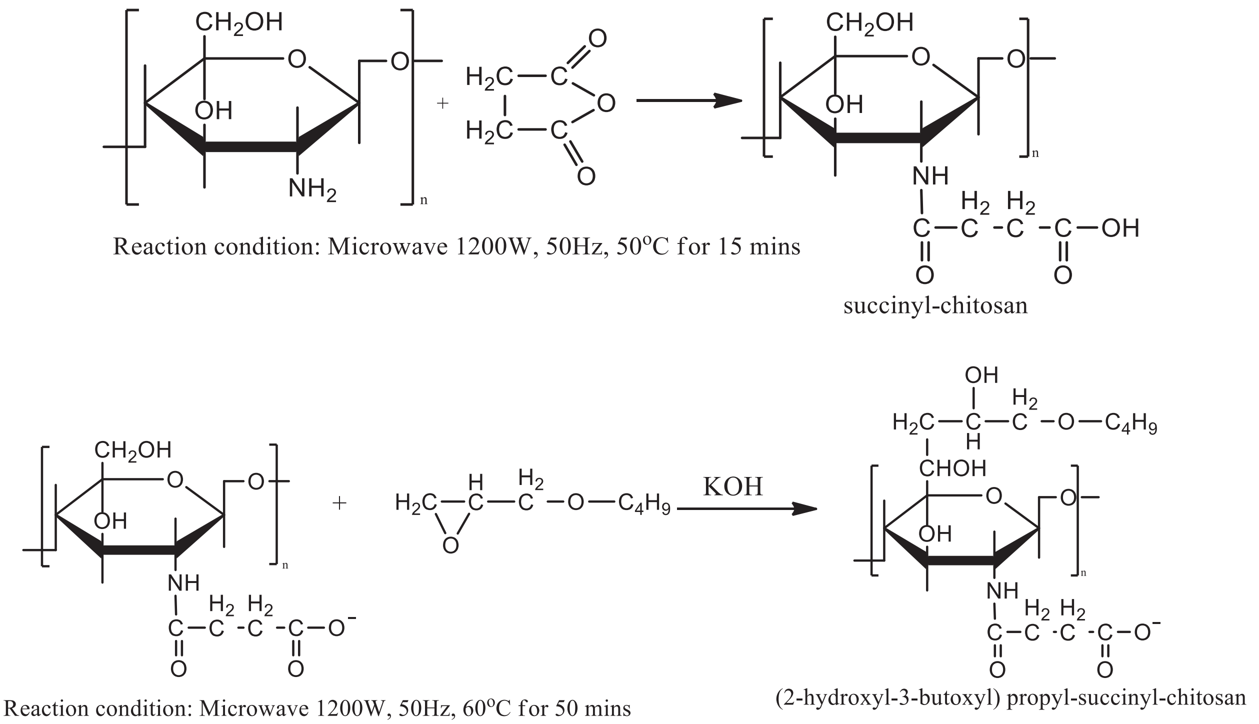
MATERIALS AND METHODS

Materials

Biologically extracted chitosan with 97% DAD and molecular weight of 50 kDa was used to carry out known synthesis. BGE and 98–99% sulfuric acid were supplied from Thomas Baker; hypo-phosphorous acid was received from S.D. Fine Chemicals; and formaldehyde (35% w/v) solution, potassium hydroxide, succinic anhydride, phthalic anhydride, acetone, methanol, propan-2-ol, and glacial acetic acid were also received from Sigma-Aldrich Chemicals and used without further purification.

HBP-SCCHS

A 1526 mg of chitosan was mixed with the 1% solution of CH_3COOH/CH_3OH in a microwave glass reactor and stirred to dissolve at room temperature for 20 min. After the addition of about 1 g of succinic anhydride, the mixture was stirred and subjected to microwave irradiation for 15 min at 50°C. In conventional synthesis, similar procedure was carried out for 3 h[30] at room temperature. The product was precipitated by adding acetone was centrifuged to separate the precipitate. The precipitate obtained was further washed with ethanol-water,



Reaction condition: Microwave 1200W, 50Hz, 50°C for 15 mins

Reaction condition: Microwave 1200W, 50Hz, 60°C for 50 mins

Figure 1: Synthesis of succinyl-chitosan (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan

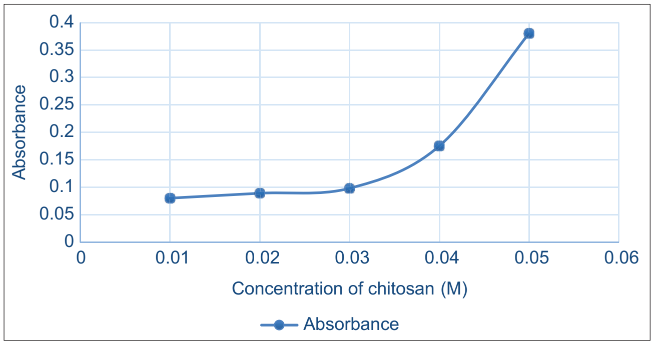


Figure 2: Plot of degree of deacetylation analysis

centrifuged, and dried in the vacuum at 50°C to get crystalline powder of SCCHS; yield: 92% [Figure 1].

A 1500 mg of prepared SCCHS was dissolved into the mixture of 20% (w/v) potassium hydroxide/isopropanol in a glass reactor, then 4.97 mL of BGE was added and mixture was irradiated under microwave at 60°C for 50 min with an interval of every 10 min. In conventional synthesis, HBP-SCCHS was synthesized by heating at 50°C for 24 h. The mixture was allowed to cool down to room temperature and obtained products were centrifuged, washed 2–3 times with acetone and isopropanol, and again centrifuged. The product obtained was purified and dried in vacuum at 55°C (92% yield of HBP-SCCHS was retained) [Figure 1 and Table S1 and S2].

Characterization of HBP-SCCHS

FT-IR spectroscopy

As FT-IR spectroscopy would give information on various functional groups present in the molecule, we were detailed FT-IR spectra of synthesized HBP-SCCHS on Shimadzu MIRacle 10 instrument. It was recorded with the aid of KBr pellets on a Shimadzu UV-1800 spectrometer. The FT-IR measurements were performed in the transmission mode. The ratio for the mixture used was 100:1 (50 mg KBr and 0.5 mg sample). Then, mixture was uniformly mixed using mortar and pestle. The spectra of chitosan samples were obtained within a frequency range of wavelength from 400 to 4000 cm^{-1}, each spectrum was an average of 45 scans with a resolution of 2 cm^{-1}.

^{1}H-NMR spectroscopy

^{1}H-NMR spectroscopy was used to characterize the molecular structure of chitosan derivatives. The ^{1}H-NMR spectra were recorded on a Bruker Avance 400 spectrometer. The SCCHS and HBP-SCCHS were dissolved in D_2O.

Deacetylation degree (DAD)

DAD and molecular weight of chitosan were computed as per the published procedure.[31] In the our synthesis, we used the enzymatically extracted chitosan; whose DAD was 97.69% as calculated using UV spectrophotometer in the following way: [32] 10–20 mg of chitosan was dispersed in 10 mL of 0.01 mol.L^{-1} HCl in a 100 mL volumetric flask. As chitosan dissolved completely, deionized water was added up to the mark. As per the standard plot, the acetyl concentration can be determined by calculating the absorbance of solution at wavelength 199 nm. DAD can be measured according to the equation:

$$\text{DAD} = 100\% - \frac{C_1}{C} \tag{1}$$

Where, C_1 is the concentration of acetyl of sample and C is sample concentration.

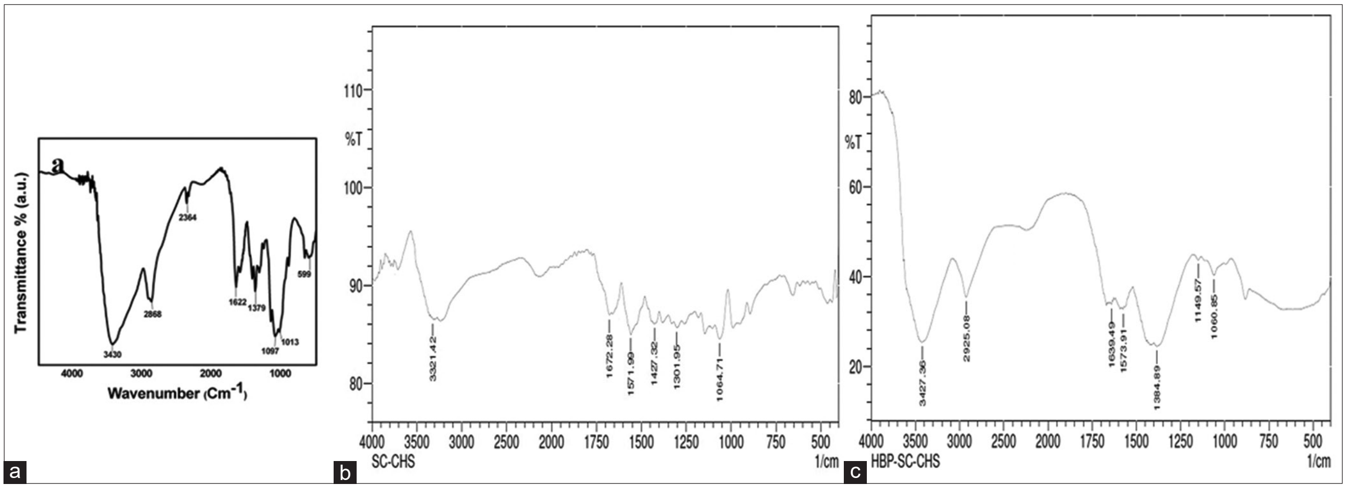


Figure 3: Fourier transform infrared spectra of (a) chitosan, (b) succinyl chitosan, and (c) (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan

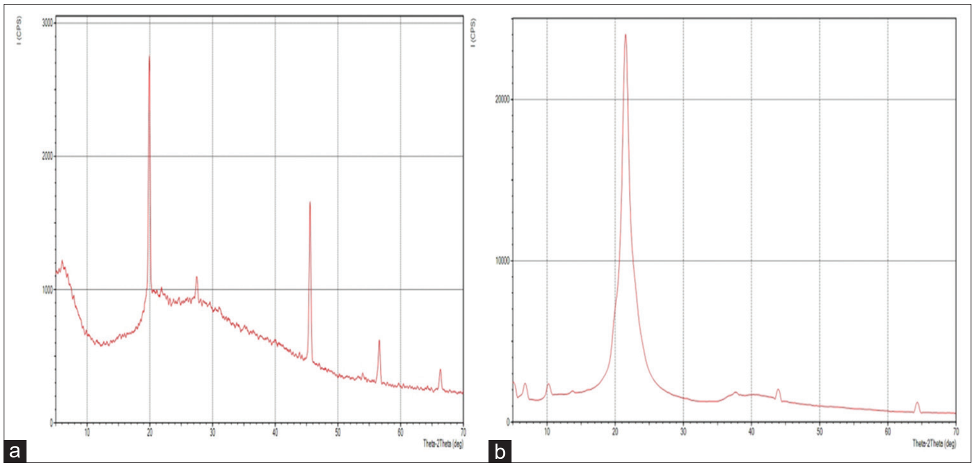


Figure 4: X-ray diffractometer diffractogram of (a) succinyl chitosan and (b) (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan

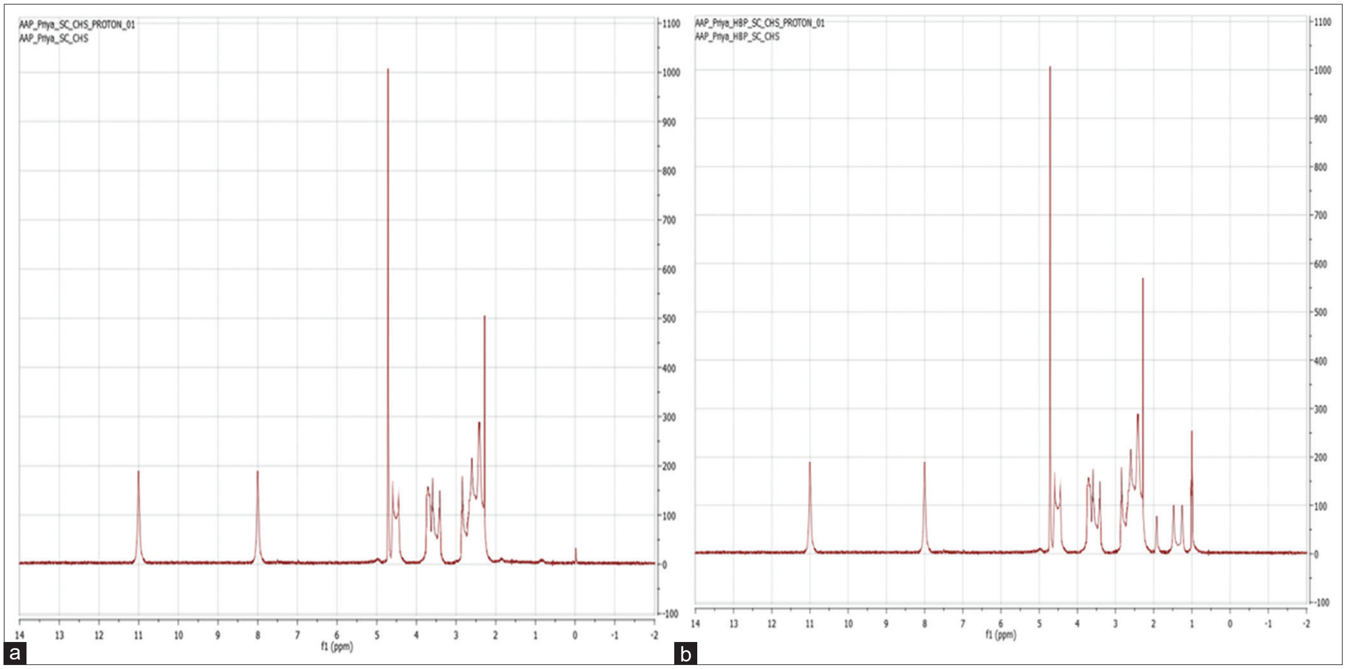


Figure 5: Nuclear magnetic resonance spectra of (a) succinyl chitosan and (b) (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan

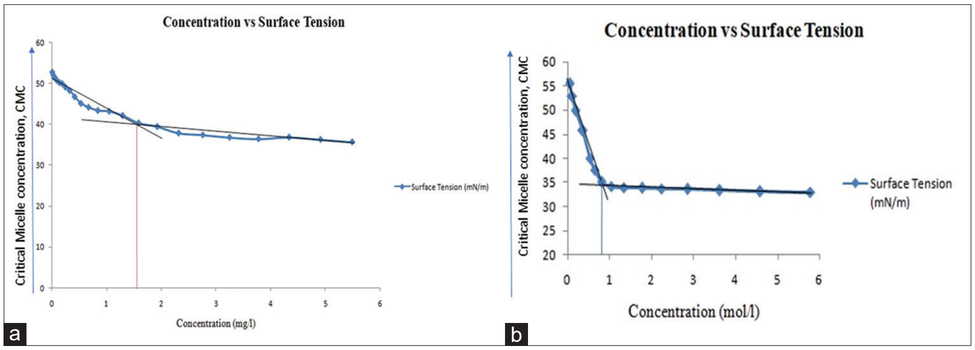


Figure 6: Critical micelle concentration graph of (a) succinyl chitosan and (b) (2-hydroxyl-3-butoxyl) propyl-succinyl-chitosan

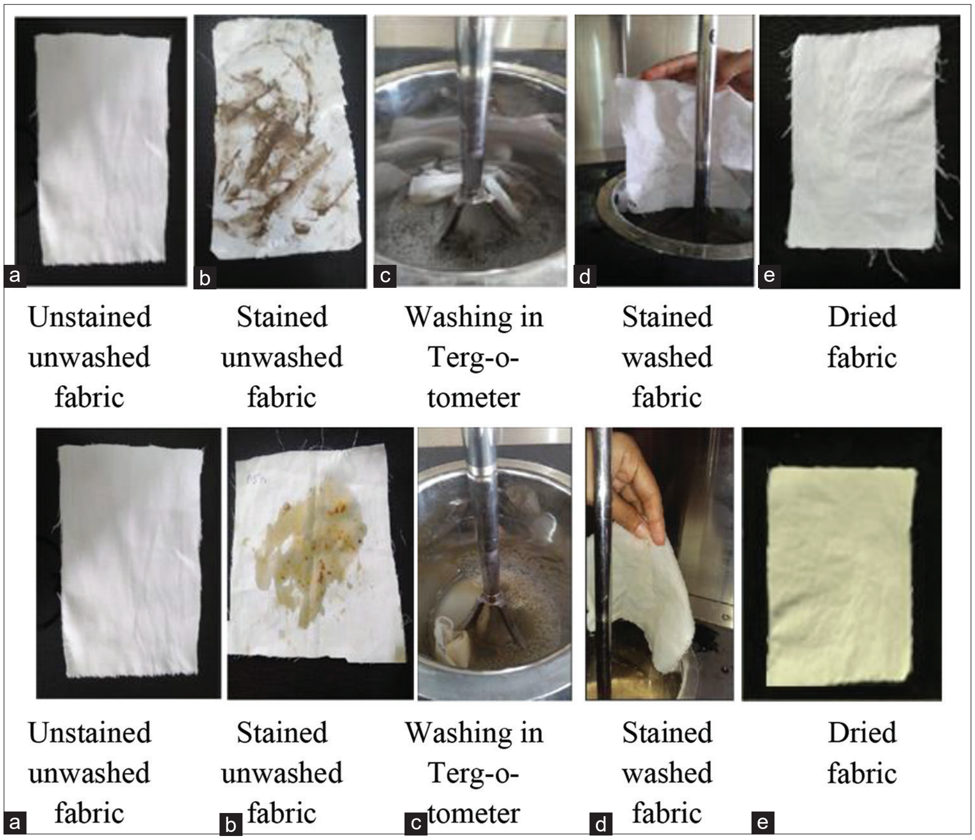


Figure 7: Detergency test of mud stain and oily stain

XRD

XRD diffractogram (XRD) pattern of chitosan sample was obtained using the X-ray (XPERT-PRO) diffractometer operating at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation (λ = 1.54060 Å). The XRD pattern was recorded as per the procedure reported in literature (in the 2θ range of 10°–80° in a fixed time mode at room temperature). Thus, with the aid of XRD analysis, crystalline nature of the obtained product was confirmed.

Thin-layer chromatography (TLC)

TLC is a useful technique to monitor a progress of chemical reactions and for assessing a purity of organic compounds. The reaction product mixture of SCCHS and HBP-SCCHS were subjected onto a pre-coated Silica Gel 60 TLC plate (Omkar Traders) and dipped in the solvent system consisting of n-butanol/water/acetic acid (5:3:1, v: v).

Ash Content Analysis

Ash content of chitosan was calculated using calcination process.[32] A 2–5 g of chitosan was combusted in the constant weight crucible in a muffle furnace at 555°C for 3 h. Then, crucible was allowed to cool in a desiccator for a ½ h and reweighted (W_1). To get constant weight (W_2) of crucible, it was firstly heated and then cooled after every 1.5 h. The ash percentage was estimated by the equation:

$$\text{Ash \%} = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \qquad (2)$$

Where, W_0 is the constant weight of crucible, W_1 is the sample weight with crucible, and W_2 is the ash weight with crucible.

Measurement of Surface Tension

The surface tension measurement was done with K1HRSS digital tensiometer (Kruss) using Wilhelmy plate method.[33,34] A platinum plate was contacted with a liquid sample and surface tension was measured as the downward force applied to Wilhelmy plate and CMC was then calculated by the plot of surface tension versus concentration.

Formulation of Liquid Laundry Detergent and Testing [SI Table S3]

Propylene glycol, anionic surfactant (HBP-SCCHS), chitosan, sodium lauryl sulfate (SLS), boric acid, anhydrous calcium chloride, and sodium chloride were dissolved in the deionized water. This mixture was then heated to dissolved SLS and boric acid. Then, pH of solution was adjusted to 7–8 using sodium hydroxide solution. The mixture was further cooled down below 100 Fahrenheit degree. Further, protease and lipase were mixed in the solution at room temperature. The detergent stability test was done by storing the detergent at 35–40°C for 30 days and it was found that there was no phase separation. Foaming power was determined by Ross-Miles method.[35] We observed 8 cm of foam in stoppered measuring cylinder and after 5 min foam level was decreased by 2 cm. Washability and color fastness tests were determined using ASTMD3050 and ASTMD4008 methods, respectively.[36]

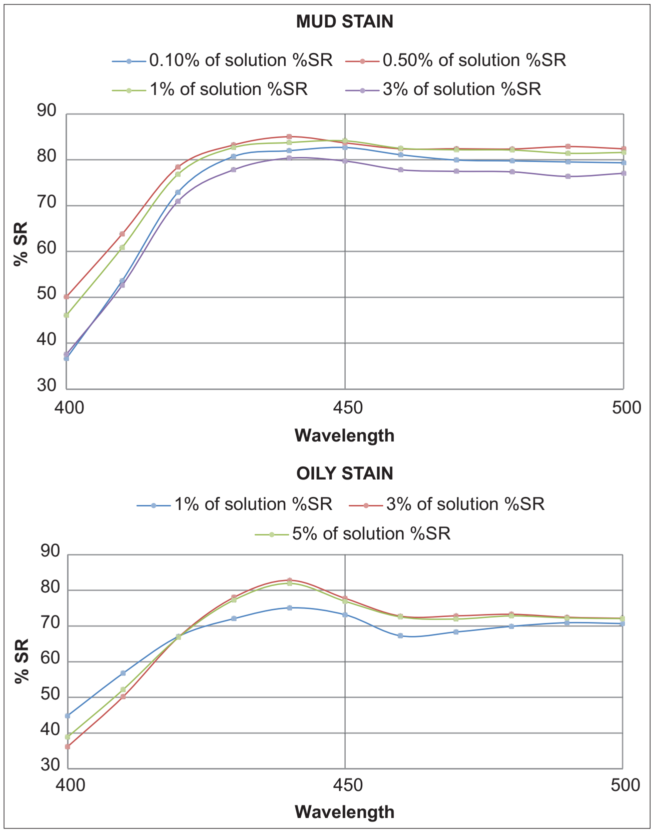


Figure 8: Plot of % stain removal versus wavelengths

Table 1: Characterization of chitosan*

DAD	Ash %	Acid Value	Amine value
97.69±0.02	57.14±0.01	2205.57±0.5	1639.45±0.21

*Each experiment was repeated twice (*n*=2) and values are reported as average±S.D

RESULTS AND DISCUSSION

Synthesis of Chitosan Derivatives Using Microwave versus Conventional Method

For our current synthesis, we optimized our reactions for both conventional and microwave modes. We noticed that microwave methods offer immediate advantages like reaction temperature reaches quickly to the desired temperature with a minimal amount of energy. As soon as the target temperature was reached, we, thus, decreased or were shut off the microwave power. This offered us added advantage of power saving, and also, most of our optimized reactions worked at extremely low or no microwave irradiation. In conventional synthesis, similar procedure was carried out for 3 h[30] at room temperature, while in microwave, we required microwave irradiation for 15 min at 50°C. This comparison is based on similar experimental conditions, such as same vessel, same reaction volume, and same microwave reactor. Moreover, microwave-assisted synthesis gave better yield of products, that is, chitosan derivatives SCCHS and HBP-SCCHS.

Characterization of Chitosan

DAD

DAD of chitosan was found to be 97.7% (calculated) according to known procedure[31] mentioned under section 2.3.3. Figure 2 indicates the plot of absorbance versus concentration; where, slope was measured as 8.3 $L^{1}mol^{-1}$.[31] Thus, according to Beer-Lambert's law, molar absorptivity was calculated as 8.3/3.7 (length of cuvette was 3.7 cm), that is, 2.24 $L^{1}mol^{-1}cm^{-1}$ and acetyl concentration (C_1) was reported as 0.2306 M.[31] Hence, DAD was computed as 97.69% [Figure 2]. Similarly, previously reported calculations for DAD were found in-line with our calculations.[31]

Ash content

The ash content was computed for two samples. From the above procedure 2.4, the ash content was found to be 57.14%. This value depicted lower values of ash content, and thus, a better quality of chitosan used comparable to the known literature.[31]

Amine value was determined by AOCS official method, Tf 1b-64 and acid value by AOCS official method, Te 2a-64.[37] The saponification value was calculated by AOCS official Db 8-48 method.[37] Tables 1 and SI. Table S1 depict the amine value, acid value, and saponification value of chitosan-derived anionic surfactant.

FT-IR analysis

On comparing the FT-IR spectra [Figure 3 and Table 2] for SCCHS and HBP-SCCHS, we noticed that the SCCHS had a new absorption peak at 1427.32 cm^{-1}, which corresponds to the SCCHS carboxyl group. The increment of amide peak (1672.28

Table 2: FT-IR of SCCHS and HBP-SCCHS

Wavelength (cm^{-1})	SCCHS		Wavelength (cm^{-1})	HBP-SCCHS	
	Assignments	**Comments**		**Assignments**	**Comments**
1064.71	C-H stretching	Strong peak	1384.89	O-H bending	Weak peak of alcohol group
1301.95	C-N stretching	Aliphatic amine band	1431.18	C-H bending	CH_3 bending band
1427.32	-COO stretching	These medium peaks show the presence of succinyl carbonyl group	1573.91	N-H stretching	Tertiary amine stretching
1672.28	C=O stretching	Conjugated acid	1639.49	C=O stretching	These peaks show the presence amide group
2152.86	N=C = O	These broad and strong peaks show the isocyanate group	2925.08	C-H stretching	Medium peak of alkyl group
3321.42	O-H stretching	Presence of alcohol	3427.36	O-H stretching	These medium peaks show the presence of free alcohol

Table 3: Testing of detergent formulation

Test	Liquid laundry detergent
pH	7.0–7.5
Stability	No phase separation
Irritation	NO
Foaming height	8 cm
Density	0.953 g/cc

cm^{-1}) and decrement of another amine peak (1427.32 cm^{-1}) depicted amidation reaction of chitosan with succinyl. Further, in the IR spectrum of SCCHS, the two peaks at 1064.7 and peak at 1030 cm^{-1} in the IR spectrum of HBP-SCCHS were credited to the methyl rocking and C-CH_3 stretching vibration, respectively.[30] These evidences denoted that the hydrophilic group and hydrophobic group were introduced to chitosan.[30] Thus, the peak at 1384.89 cm^{-1} in FT-IR spectra might be coming from aliphatic alcohol Table 2. IR spectra [Figure 3] indicate functional groups present in the synthesized SCCHS and HBP-SCCHS.

XRD analysis

X-ray diffraction is a common technique used for the study of atomic spacing and the crystal structure. With the help of this technique, one can get the atomic and molecular structure of a compound. The crystalline nature of SCCHS and HBP-SCCHS chitosan derivatives was investigated by XRD. Chitosan exhibited characteristic crystalline peak at $2\theta = 20.20°$ as reported in several literature (which, herein, were little shifted to a higher diffraction angle).[38] At the same time, chitosan contained only one broad diffraction peak centered at $2\theta = 20.20°$. Similar studies also exhibited different diffraction peak at $2\theta = 20°$, revealing a typical identification for semi-crystalline chitosan.[39] The 2θ values of the chitosan derivatives were found to be at 20° for SCCHS and 22° for HBP-SCCHS, typical to the reported values for chitosan,[39], and thus, they indicated the presence of crystalline nature of chitosan derivatives [Figure 4].

^{1}H-nuclear magnetic resonance (^{1}H-NMR) analysis

^{1}H-NMR technique is used for determining the content and purity of sample as well as its molecular structure. ^{1}H-NMR technique helps us to determine the number of protons present in a compound. SI. Table S2 shows the structural confirmation of the anionic surfactant HBP-SCCHS on the basis of their chemical shift. The proton NMR analysis was used for the final confirmation of the structure of SCCHS and HBP-SCCHS, which indicated the formations of chitosan derivatives using microwave irradiation [Figure 5].

TLC

TLC is a useful technique to monitor a progress of chemical reactions and for assessing a purity of organic compounds. Solvent system would always play a very important role in TLC analysis. The TLC plate shown in Figure S1 was scanned, digitized, and analyzed using UV chamber.

The behavior of every component in TLC is determined by a quantity called as retention factor (R_f) and is expressed in a decimal fraction. The R_f is defined as the distance travelled by the compound from the baseline divided by the distance travelled by solvent from the baseline (the solvent front).

$$R_f = \frac{distance\,travelled\,by\,component}{distance\,travelled\,by\,solvent} \qquad (3)$$

From SI. Figure S1, it is clear that Rf for SSCHS and HBP-SCCHS was obtained at 0.879 and 0.744, respectively.

Surface Tension

The procedure for measuring the surface activity was followed from several literature.[40-45] It can be seen from Figure 6, that with the increase of degree of substitution of the SCCHS, the surface tension observed to be decreasing at the same concentration of the chitosan derivatives (as there are more hydrophobic groups get to the surface of the solution) [Table S1]. The surface tension of SLES at CMC for a single surfactant was measured to be 34 mN/m (literature – above 28 mN/m).[40] The surface activity was found to be nearly equal to the commercial anionic surfactant like sodium lauryl ether sulfate (SLES) having CMC (0.80 mM).[41]

CONCLUSION

We prepared chitosan-derived anionic surfactants, SCCHS and HBP-SCCHS using greener route, that is, microwave irradiation. The FT-IR and ^{1}H-NMR spectra were confirmed the successful synthesis of the chitosan derivative, SCCHS and HBP-SCCHS. This route offered us several advantages including the ease of synthesis, higher yields, minimum time for reactions, and higher product purity. As we know that, chitosan is insoluble in aqueous neutral and basic media. To overcome this problem, water-soluble derivatives of chitosan were prepared and tested for surfactant property. Results for surface tension of SCCHS and HBP-SCCHS showed that these derivatives can act as a good wetting agent; therefore, we can use it in a formulation of liquid laundry detergents. Thus, chitosan-based anionic surfactants can also be used in various cosmetics applications such as body wash, face wash, and shower gel.

APPLICATION

The synthesized anionic surfactant, that is, chitosan derivative (HBP-SCCHS) was used in the formulation (as per section 2.6, SI. Table S3) of liquid laundry detergent. An excellent foam was retained with liquid laundry detergent.

Testing of Detergent [Table 3]

Terg-o-tometer was used for optimization of washing condition and assessment of brightening, softening, and foaming. Initially, the mud stain and oil stain were applied on fabric, and then, it was washed up in terg-o-tometer using various concentration of liquid detergent (0.1%, 0.5%, 1%, 3%, and 5%) for 25 min at 35°C and at 75 RPM [Figure 7]. Then, washed fabric was subjected to reflectometer, and % SR (stain removal) was determined. Using the equation:

$$\%\mathrm{SR} = \left(\frac{Rw - Ru}{Rn - Ru}\right) \times 100 \tag{5}$$

Where, R = Reflectance, n = normal unstained unwashed fabric, u = stained unwashed fabric, and w = stained washed fabric.

This detergency test showed the best SR (stain removal) for mud stain fabric at 0.5% concentration and oily stain fabric at 3% concentration of liquid detergent [Figure 8 and SI Table S4]

ACKNOWLEDGMENT

The authors thank Asst. Prof. Amit. P. Pratap, Head of the Department of Oils, Oleochemicals and Surfactant Technology and also thankful to Institute of Chemical Technology, Mumbai.

REFERENCES

1. Lee M, Honga K, Kajiuchi T, Yang J. Synthesis of chitosan-based polymeric surfactants and their adsorption properties for heavy metals and fatty acids. Int J Biol Macromol 2005;36:152-8.
2. Gupta KC, Jabrail FH. Glutaraldehyde cross-linked chitosan microspheres for controlled release of centchroman. Carbohydr Res 2007;342:2244-52.
3. Carrier O, Covis R, Marie E, Durand A. Inverse emulsions stabilized by a hydrophobically modified polysaccharide. Carbohydr Polym 2011;84:599-604.
4. Glass JE. Hydrophilic polymer performance with environmental acceptance. In: Advances in Chemistry Series. Vol. 248. Washington, DC: American Chemical Society; 1996.
5. Petit C, Reynaud S, Desbrieres J. Amphiphilic derivatives of chitosan using microwave irradiation. Toward an eco-friendly process to chitosan derivatives. Carbohydr Polym 2015;116:26-33.
6. Arvanitoyannis I, Nakayama A, Aiba S. Chitosan and gelatin based edible films: State diagrams, mechanical and permeation properties. Carbohydr Polym 1998;37:371-82.
7. Gupta KC, Ravikumar MN. Drug release behavior of beads and microgranules of chitosan. Biomaterials 2000;21:1115-9.
8. Shiraishi S, Imai T, Otagiri M. Controlled release of indomethacin by chitosan-polyelectrolyte complex: Optimization and *in vivo/ in vitro* evaluation. J Control Release 1993;25:217-25.
9. Kaur S, Dhillon GS. Recent trends in biological extraction of chitin from marine shell wastes: A review. Crit Rev Biotechnol 2015;35:44-61.
10. Pal J, Verma HO, Munka VK, Maurya SK, Roy D, Kumar J. Biological method of chitin extraction from shrimp waste an eco-friendly low cost technology and its advanced application. Int J Fish Aquat Stud 2014;1:104-7.
11. Shelke PB, Mali SN, Chaudhari HK, Pratap AP. Chitosan hydrochloride mediated efficient, green catalysis for the synthesis of perimidine derivatives. J Heterocycl Chem 2019;56:3048-54.
12. Gadgey K, Bahekar A. Studies on extraction methods of chitin from crab shell. Int J Mech Eng Technol 2017;8:220-31.
13. Mourya V, Inamdar N. Chitosan-modifications and applications: Opportunities galore. Reacti Funct Polym 2008;68:1013-51.
14. Inamdar N. Chitosan-modifications and applications: Opportunities galore. Reacti Funct Polym 2008;68:1014-5.
15. Jain A, Gulbake A, Shilpi S, Jain A, Hurkat P, Jain S. A new horizon in modifications of chitosan: Syntheses and applications. Crit Rev 2013;30:92.
16. Mali SN, Pratap AP. Improved synthesis of sophorolipids, biosurfactants using industrial by-products and its practical application. In: Tenside Surfactants Detergents; 2021.
17. Pratap AP, Datir K, Mane S, Shukla G. Synthesis of dimeric surfactant based on neem fatty acid and its characterization. Chem Pap 2021;75:1981-991.
18. Parikh R, Godse S, Pawar N, Pratap A. Synthesis and characterization of 2-Di-methyl amino ethyl laurate betaine surfactant. Vol.49. In: Tenside Surfactants Detergents; 2021. p. 220-9.
19. Dane F, Halide A, Leventer S. Phytotoxic effects of dimeric cationic surfactant gemini (16-2-16), (16-6-16) and (16-10-16). In: International Conference on Chemical, Environment and Biological Sciences; 2014. p. 65.
20. Yuan C, Xu Z, Fan M, Liu H, Xie Y, Zhu T. Study on characteristics and harm of surfactants. J Chem Pharm Res 2014;6:2233-7.
21. Corazza M, Lauriola MM, Zappaterra M, Bianchi A, Virgili A. Surfactants, skin cleansing protagonists. J Eur Acad Dermatol Venereol 2010;24:1-6.
22. Siyal AA, Shamsuddin MR, Rabat NE, Zulfiqar M, Man Z, Low A. Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution. J Clean Prod 2019;229:232-43.
23. Huacai G, Wan P, Dengke L. Graft copolymerization of chitosan with acrylic acid under microwave irradiation and its water absorbency. Carbohydr Polym 2006;66:372-8.
24. Liu L, Li Y, Fang YE, Chen L. Microwave-assisted graft copolymerization of e-caprolactone onto chitosan via the phthaloyl protection method. Carbohydr Polym 2005;60:351-6.
25. Liu L, Li Y, Li Y, Fang YE. Rapid N-phthaloylation of chitosan by microwave irradiation. Carbohydr Polym 2004;57:97-100.
26. Matahwa H, Ramiah V, Jarrett WL, Mcleary JB, Sanderson RD. Microwave assisted graft copolymerization of N-isopropylacrylamide and methyl acrylate on cellulose: Solid state NMR analysis and CaCO3 crystallization. Macromol Symp 2007;250:50-6.

27. Mishra S, Rani GU, Sen G. Microwave initiated synthesis and application of polyacrylic acid grafted carboxymethylcellulose. Carbohydr Polym 2012;87:2255-62.
28. Horchani H, Chaâbouni M, Gargouri Y, Sayari A. Solvent-free lipase catalyzed synthesis of long-chain starch esters using microwave heating: Optimization by response surface methodology. Carbohydr Polym 2010;79:466-74.
29. Moran M, Pinazo A. “Green” Amino Acid-Based Surfactants. London, United Kingdom: The Royal Society of Chemistry; 2004. p. 233-4.
30. Sui W, Wang Y, Dong S, Chen Y. Preparation and properties of an amphiphilic derivative of succinyl-chitosan. Colloids Surf A Physicochem Eng Aspects 2008;316:171-5.
31. Singh PS, Shaikh A, Deshmukh A, Pratap AP. Microwave assisted synthesis of cationic amino sugar surfactants. Vol. 57. In: Tenside Surfactants Detergents; 2020. p. 265-72.
32. Yuan Y, Chesnutt B, Haggard W, Bumgardner J. Deacetylation of chitosan: Material characterization and *in vitro* evaluation via albumin adsorption and pre-osteoblastic cell cultures. Materials 2011;4:1399-416.
33. Ramé E. The interpretation of dynamic contact angles measured by the Wilhelmy plate method. J Colloid Interface Sci 1997;185:245-51.
34. Moghaddam MS, Wålinder ME, Claesson PM, Swerin A. Multicycle Wilhelmy plate method for wetting properties, swelling and liquid sorption of wood. Langmuir 2013;29:12145-53.
35. Rosen MJ, Solash J. Factors affecting initial foam height in the Ross-Miles foam test. J Am Oil Chem Soc 1969;46:399-402.
36. Cohen L, Vergara R, Moreno A, Berna JL. Linear alkylbenzene sulfonate detergency behavior in water containing magnesium ions. J Am Oil Chem Soc 1993;70:723-6.
37. Bistline RG, Linfield WM, Pfeffer PE, Piotrowski EG, Sonnet PE, Wise WB. Reaction of β-aminoamides with aromatic aldehydes. J Am Oil Chem Soc 1987;64:741-3.
38. Yen MT, Mau JL. Physico-chemical characterization of fungal chitosan from shiitake stipes. LWT Food Sci Technol 2007;40:472-9.
39. Li Q, Zhou J, Zhang L. Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers. J Polym Sci B Polym Phys 2009;47:1069-77.
40. Ahmad A, Yeong SK, Ismail R, Ooi TL, Ahmad S. Synergistic effect between sodium lauryl sulphate and sodium lauryl ether sulphate with alkyl polyglycoside. J Oil Palm Res 2007;19:332.
41. Aoudia M, Al-HaDADbi B, Al-Harthi Z, Al-Rubkhi A. Sodium lauryl ether sulfate micellization and water solubility enhancement towards naphthalene and pyrene: Effect of the degree of ethoxylation. J Surf Deterg 2010;13:103-11.
42. Shaban SM, Fouda AS, Rashwan SM, Ibrahim HE, El-Bhrawy MF. Synthesis and characterization of newly cationic surfactants based on 2-(2-(dimethylamino) ethoxy) ethanol: Physiochemical, thermodynamic and evaluation as biocide. J Mol Liq 2016;221:224-34.
43. Shaban SM, Aiad I, El-Sukkary MM, Soliman EA, El-Awady MY. Synthesis, surface, thermodynamic properties and biological activity of dimethylaminopropylamine surfactants. J Ind Eng Chem 2014;20:4194-201.
44. El-Sukkary MM, Aiad I, Deeb A, El-Awady MY, Ahmed HM, Shaban SM. The preparation and characterization of some novel quaternary iminium salts based on schiff-base as a corrosion inhibitor. Pet Sci Technol 2010;28:1158-69.
45. Aiad I, EL-Sukkary MM, El-Deeb A, El-Awady MY, Shaban SM. Surface and biological activity of some prepared iminium surfactants based on Schiff bases. J Surf Deterg 2013;16:243-50.