# Study of Starch Based Biodegradable Polymeric Surfactants for Better Cleansing Activity

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*Authors' contributions*

*This work was carried out in collaboration between all authors. Authors MIHM and MMH designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors MMH and MRS managed the analyses of the study. Authors MMH and MRS managed the literature searches. All authors read and approved the final manuscript.*

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## ABSTRACT

In the present case, biodegradable starch interactions with various surfactants have been studied for the investigation of ability and cleansing activity of the starch-surfactant-water system. The surfactants investigated were sodium dodecyl sulphate (SDS) sodium octanoate (NaOct), cetyltrimethyl ammonium bromide (CTAB) and tween20. The degree of substitution (DS) of starch is 0.8 and the concentrations of starch were varied from 0.01 to 1% wt/v. The effect of mixing on the micellisation of the ternary surfactant solutions can be described to a good approximation by taking into account only the effects of the amount difference between the hydrocarbon chains length. Mixed micelle formation with starch depends on the chain-length in hydrocarbon in hydrocarbon difference in the same way as for starch-surfactant micelle. Aggregation of the mixed micelles of the surfactants and the polymer coils produced a gel-like complex phase. The water content of the gel phase in equilibrium in aqueous solution increased when the chain-length difference between the two surfactants increased. The more surface-active component is strongly enriched in the polymer complexes of gels

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and it showed maximum cleansing activity of respective detergent. The experimental results of viscosity, surface tension and other physical properties indicated that addition of starch in detergent as soap filler these properties have changed. The complexes were analyzed and characterized by FTIR, XRD and SEM and the complexes exhibited excellent emulsifying efficiency and surfactants performance properties with this biodegradable starch polymer.

## 1. INTRODUCTION

The cleansing activity of soap-detergent is one of the most important phenomena in our daily life. Thus the improvement activity of soap-detergent is obviously required for better quality and performance of surfactants. The biodegradable polymers derived from natural resources are potentially very interesting substitutes for non-biodegradable petroleum-based polymers. An attractive field of application of these polymers is their use as packaging materials. For the current petrochemical based products recycling is often neither practical nor economically feasible [1].Natural polymers such as starch, cellulose or proteins are potentially very interesting starting materials for biodegradable packaging materials.

In particulars, starch is an attractive as it is relatively cheap and abundantly available. However, the general picture emerging from these studies is that in dilute solution the surfactant molecules adsorb polymer chains as micellar or micelle-like clusters. A general phenomenon in system of polyelectrolytes and oppositely charged surfactant is that complexes of these components separate as a water-swollen phase in equilibrium with very dilute aqueous solution. Generally, the rich phase behavior of surfactants in water is also characteristic of starch-surfactant complexes in contact with water. Thus, in complexes, the interactions may be intra- and/or intermolecular. The balance depends on the structural parameter necessary for softening the polymer, such as the nature, length and content of hydrophobic groups, their distribution along the starch, the hydration capacity, the degree of polymerization, polymer concentration and on other parameters such as salinity, pH and organic co-solvents [2,3]. Among the associated polymers, amphiphilic polysaccharides with a natural non-toxic and biodegradable carbohydrates are of particular interest. They were prepared by the hydrophobic modification of a variety of polysaccharides, such as corn, potato [4], hydroxyethyl cellulose, carboxymethyl cellulose [5,6] and pullulan [7]. Increasing interest has been focused on the structure–solution property relationship of amphiphilic polysaccharides [8-10]. The associative behaviors of hydrophobically modified carboxymethyl cellulose and carboxymethyl pollulan were studied after the amidation of these polysaccharides in DMSO [6,7]. In a previous study, the hydrophobization of various polysaccharides were investigated, such as hydroxyl ethylcellulose [11], carboxymethyl cellulose [12], xylan [13], and carboxymethyl starch [14,15] by the esterification of hydroxyl groups using classical (with acyl chloride and mixed anhydride) and unconventional methods. The interactions of surfactants with cationised cellulose, has been studied by Goddard et al. [16,17] and nonionic cellulose ethers have been subject of extensive studies by Piculell and Lindman [18]. The structure of starch is very similar to cellulose, but the difference on the bindings, which link the mono glucose units to form the polymer, makes their chemical behavior very different. The polymer chains in starch are much more flexible than in cellulose, making the polymer more soluble in different solvents. The polymer chains of amylopectin in starch are also branched, whereas cellulose has completely straight chain. Thus, actually starch is very different material to cellulose despite of their chemical similarity.

The Infrared spectra of starch and related compounds have been studied for a long time by a number of authors [19,20]. These authors studied the infrared spectra in the detection of chemical changes in starch and some other starch-surfactant derivatives and investigated the effect of hydrogen bonding and change in crystalline structure on the infrared spectrum of starch. Starch-surfactants complex interactions of H- atom of starch within the surfactant molecule by the H-bonding process are now subject to IR absorption of the functional groups which may vary over a wide range.

From the above mentioned features, it can be pointed out that many researchers emphasized on this field. With the passes of time, many academic aspects such as, chemistry, chemical reactions, bond formation of starch-surfactants interaction are still open for discussion. The purpose of the present investigation is to explore the effect of starch interaction on various surfactants for better understanding the mechanism of starch and surfactant complexes studied by the ternary phase diagram, interfacial surface tension and viscometric measurement. The instruments like XRD, SEM, FTIR etc. were used to characterized the product samples in the present investigations.

## 2. MTERIALS AND METHODS

### 2.1 Materials

Starch was purchased from UNI-CHEM, China and its degree of substitution (DS) was 0.80.Starchsolution was prepared by heating in water in an autoclave at 120ºC for 30min. All solutions were prepared within 24h before measurements were performed. The surfactants sodium dodecyl sulphate (SDS), N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB), sodium octanoite (NaOct) were purchased as analytical grade and were used without further purification. The water used was ion exchanged and distilled. Its conductivity and reduced viscosity were 2.0 µs and 4.0 $dm^3$/mol, respectively and its surface tension was $71.5×10^{-3}±0.5$N/m at $30^o$C. All other chemicals were analytical grade and used without further purification.

### 2.2 Methods

#### 2.2.1 Surface and interfacial tension measurements

Surface tension was measured with a drop weight method (Stalagmometer Instruments). In the calculation of surface tension, the correction factors of Huh and Mason [21] were used. There producible results between measurements of the same sample was ±0.5N/m. The results of the surface tension measurement were calculated from the equation (1) below:

$$\gamma = \frac{mg}{2\pi r f}$$

(1)

where, f is equal to $\frac{1}{v^3}$ ,v is the volume of the drop and r is its radius, mg is the weight of falling drop and $\gamma$ is its surface tension.

A drop of the weight (mg) given by the above equation has been designated as the ideal drop. Repeated measurements (2-4 times) were conducted on each sample from which

equilibrium surface or interfacial tension values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to running tests with the starch solutions, the instrument was calibrated with water and then checked by measuring the interfacial tension between water and pure starch.

### 2.2.2 Viscosity

Viscosities were determined with an Ostwald viscometer according to British standard (Fisher Scientific TM200) with a fluctuation of ±0.1$^o$C was used. The flow time was recorded by a timer accurate up to ±0.01 second. At certain surfactant/starch ratio the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements. The results of the viscosity values were calculated from equation (2) below:

$$\eta_{red} = \frac{\frac{(t - t_0)}{t_0}}{c}$$

(2)

Where t is the measured efflux time of solutions and $t_0$ is the efflux time of the pure solvent (water) and C is the weight concentration of the surfactant, starch & surfactant mixed polymer.

### 2.2.3 SEM analysis

Scanning Electron Microscope (SEM) of potato starch, surfactant and starch-surfactant complexes were less than 4% moisture content before examined. Dried sample was taken onto the double-sided adhesive tape attached to the specimens tub. The excess sample was removed and the sample was placed in fine coater of gold coating for 150 sec. The coated sample was then placed in the sample chamber of the SEM. The sample was examined at a magnification of 2,500 and 6,000 with the accelerating voltage of 10 kV.

### 2.2.4 FTIR spectroscopic analysis

Potato starch is a polymer, cetyltrimethyl ammonium bromide (CTAB) is a cationic surfactant and sodium dodecyl sulphate (SDS) is a anionic surfactant. 0.2g sample was dried in an electric oven at 105ºC for 30 min. Tween 20 is a non-ionic highly viscous liquid. About 10ml sample was taken into glass tray and dried at 105ºC for 2h. Sample with KBr was ground with a mortar-pastle and a pellate was made. FTIR of the KBr pellate was measured with Shimadzu FTIR-470 infra-red spectrophotometer between 400 - 4000 cm$^{-1}$.

## 3. RESULTS AND DISCUSSION

## 3.1 Surface Active Properties

Some of the prepared starch-surfactant mixtures have lowered the surface tension of water, namely at lower concentration of the sample Table1. The functional properties of some of the prepared starch-surfactant mixtures (CTAB, SDS, Tween 20, NaOCt) have been analyzed for better cleansing activity in between ionic and non-ionic surfactants. Here three types of surfactants have been used such as cationic (CTAB), anionic (SDS, NaOct) and

non-ionic (Tween 20) surfactant, and starch mixed surfactant solutions were tested for emulsifying efficiency, washing power and anti-redepositive efficiency. The emulsifying efficiency was characterized by the stability of the paraffinic Tween20/ water emulsion and other surfactant mixture at definite ratio. The results summarized in Table 2 shows that some of the surfactant made emulsions of the oil/ water type stable even after 24h. Starch mixed ionic surfactant (CTAB, SDS) cleansing efficiency was comparable to that of the commercial emulsifier Tween20. Some of the tested mixture showed excellent washing power exceeding that of the anionic detergent, namely SDS containing dodecyl chains. The anti-redepositive efficiency was higher than the starting SDS, but moderate in comparison to starch used as a co-builder in detergents [22].

**Table 1. The value of surface tension of all types of surfactants with added starch**

| Log conc. of surfactant solution (%) | Conc. of surfactant solution, Mol/dm$^3$ (M) | Surface tension of SDS mixed with starch soln. (N/m) | Surface tension of CTAB mixed with starch soln. (N/m) | Surface tension of Tween 20 mixed with starch soln. (N/m) | Surface tension of NaOct mixed with starch soln. (N/m) |
|---|---|---|---|---|---|
| -2.00 | 0.01 | 49.11 | 49.19 | 49.11 | 48.88 |
| -1.69 | 0.02 | 48.02 | 47.15 | 47.19 | 47.08 |
| -1.52 | 0.03 | 45.35 | 45.67 | 45.75 | 45.34 |
| -1.39 | 0.04 | 44.31 | 44.89 | 44.61 | 43.38 |
| -1.30 | 0.05 | 43.13 | 44.15 | 43.63 | 42.80 |
| -1.22 | 0.06 | 42.95 | 43.37 | 42.84 | 42.24 |
| -1.15 | 0.07 | 42.73 | 42.69 | 42.45 | 41.98 |
| -1.09 | 0.08 | 42.55 | 42.46 | 42.05 | 41.88 |
| -1.04 | 0.09 | 42.52 | 42.45 | 42.05 | 41.86 |
| -1.00 | 0.10 | 41.51 | 42.41 | 42.07 | 41.86 |

**Table 2. Critical micelle concentration of binary surfactant mixtures of SDS, CTAB, Tween 20 and NaOCt**

| Mole fraction | SDS/ CTAB | SDS/ Tween 20 | CTAB/ Tween 20 | NaOCt/ CTAB | NaOCt/ Tween 20 | SDS/ NaOCt |
|---|---|---|---|---|---|---|
| 0 | 0.98 | 0.071 | 0.071 | 25.0 | 23.0 | 8.32 |
| 0.17 | 1.10 | 0.074 | 0.081 | 28.2 | 27.9 | 9.75 |
| 0.25 | 1.26 | 0.090 | 0.092 | 30.1 | 28.6 | 10.5 |
| 0.50 | 1.60 | 0.128 | 0.122 | 39.6 | 37.2 | 15.0 |
| 0.75 | 2.32 | 0.212 | 0.236 | 52.7 | 56.3 | 24.4 |
| 0.83 | 3.03 | 0.296 | 0.406 | 62.3 | 72.3 | 32.2 |
| 0.91 | 3.67 | 0.403 | - | 73.2 | 76.5 | - |
| 1.0 | 95.5 | 0.993 | 96.7 | 95.5 | 97.5 | 95.5 |

## 3.2 Analysis by Viscometric Measurement

Fig.1 shows the reduced viscosity of starch solutions containing different surfactant mixtures. The viscosity drop occurs at lower concentration as the hydrocarbon chain length of the second surfactant is increased. Thus, the interactions depend markedly on the surface activities of the surfactants. The viscosity increases when excess surfactant begins to dissolve and at the same time, the added excess surfactant begins to form free micelles. Thus, the result is an increased viscosity. The surfactant concentrationat whichthe sudden viscosity reduction occurred and increased, when the NaOct/CTAB molar ratiois decreased.

The viscosity becomes minimum level due to the charge neutralization at a higher surfactant concentration than with the pure NaOct. From comparison studies at a fixed concentration of starch but different concentrations of surfactant, it has been found that at a certain concentration of surfactant surface tension value is minimum which indicates maximum cleansing activity appeared at the mentioned point. Fig. 2 shows the variation of molar ratio of two surfactants; the log concentration vs reduced viscosity. With an increase of log concentration of molar ratio the reduced viscosity decreased. Such behavior confirms the existence of a strong interactions between starch and surfactant. It can also be seen from Figs. 3 and 4 that log conc vs surface tension values plot at fixed Critical micelle concentrations, the value of surface tension is minimum but after increasing log conc the surface tension curve is level off. Fig. 3 shows the surface tension of solutions of NaOct and NaOct/CTAB mixtures in 0.01 wt.% starch solutions as a function of the surfactant concentration. Critical micelle concentrations are indicated by sudden changes in the slope of the curves. When part of the NaOct is replaced by CTAB, the critical micelle concentration (CMC) increases with an increase in mole fraction of the short-chain surfactant. At concentration considerably above those values corresponds to charge equivalence between the amounts of surfactant and starch, a complex phase containing high concentrations of surfactants and polymer is formed. The phase separation can be observed visually as a clouding of the sample. The two phase area is represented by a dashed line in the Figs. 1 and 2. Phase separation takes place at higher surfactant concentrations when the fraction of NaOct increases (Fig. 2). Increasing the mole fraction of NaOct above 0.83 does not significantly affect the CMC, but the two phase area extends to higher concentrations. Fig. 3 shows the surface tension when a mixture of NaOct and shorter-chain surfactant is added (1:1 mole ratio) at constant starch concentration. Although the effect is not very marked, the CMC is always higher than for pure NaOct. The shift decreases when the chain length of the second surfactant increases. The concentration at which the gel phase separation increases in the order NaOct<CTAB<SDS<Tween 20. Redissolution, which is not complete with this highly charged starch (DS=0.80), also takes place at a slightly higher concentration the shorter is the chain length of the second surfactant. Here it is mentioned that starch is obtained from nature, but detergent is chemical substance which is harmful for water living organisms, and but the product is biodegradable hence it is also eco-friendly.
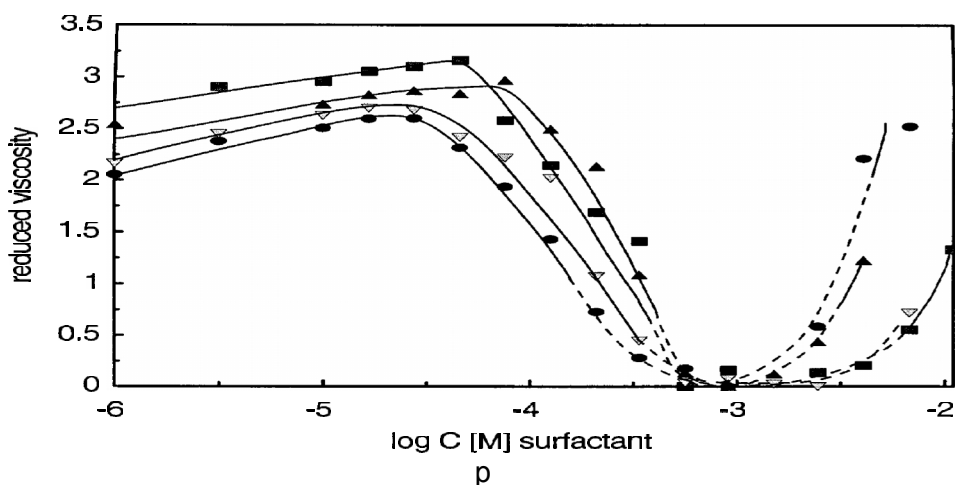


**Fig. 1. Reduced viscosities of solutions of potato starch (0.01 wt.%, DS=0.80) and NaOct/second surfactant mixtures. The surfactants were NaOct (●), NaOct/CTAB (▼), NaOct/SDS (♦) and NaOct/Tween 20 (▲). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The two-phase domain is indicated by the dotted line**
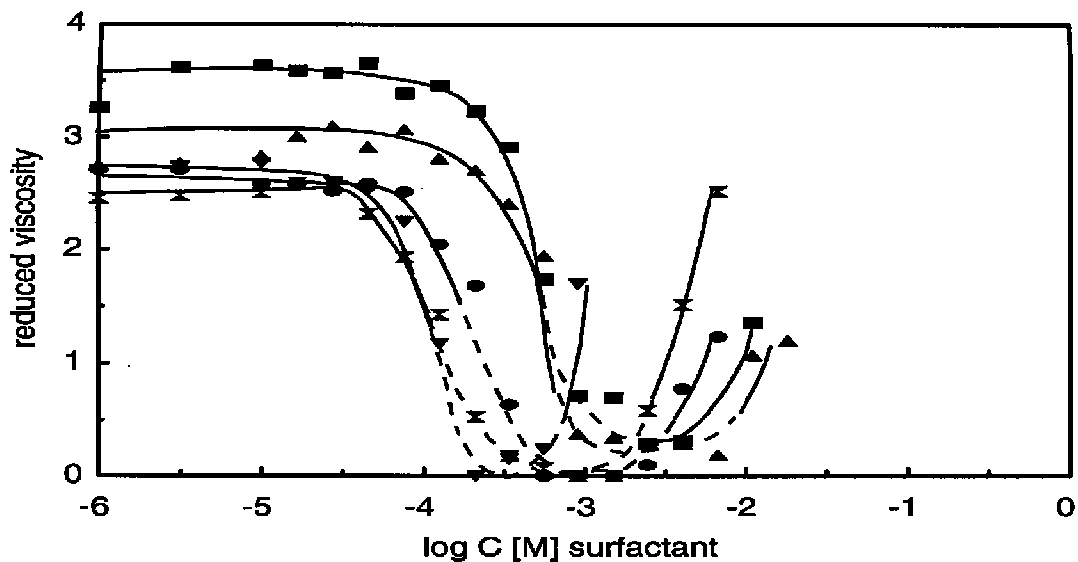
**Fig. 2. Reduced viscosities of solutions of starch (0.01 wt %, DS=0.80) and SDS/CTAB mixtures. The molar ratios of the surfactants were 1:0 (▼), 3:1 (✕), 1:1 (●), 1:3 (▲) and 1:5 (♦). The two-phase domain is indicated by the dotted line**
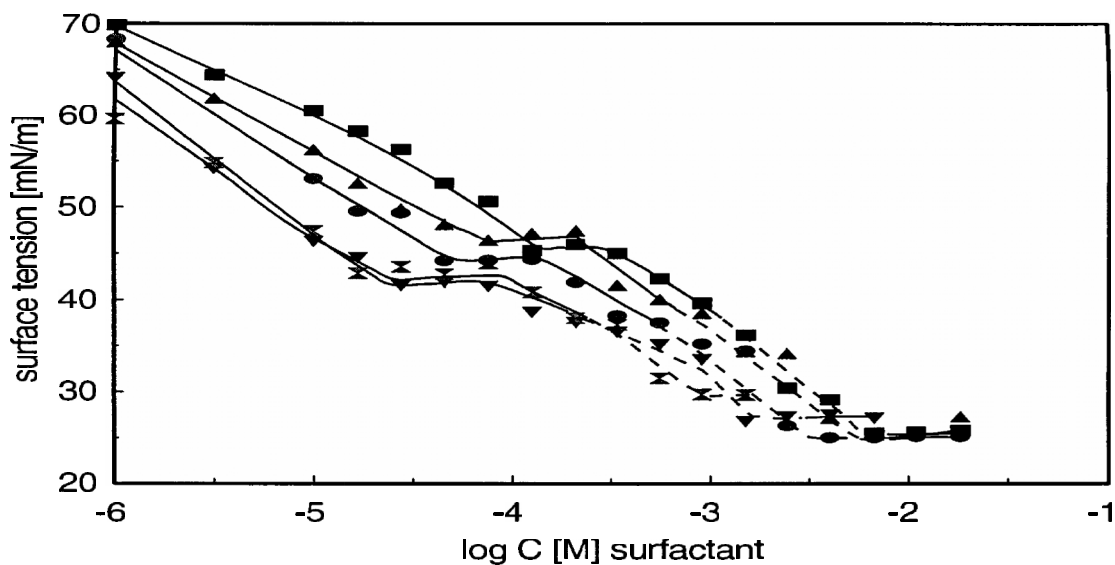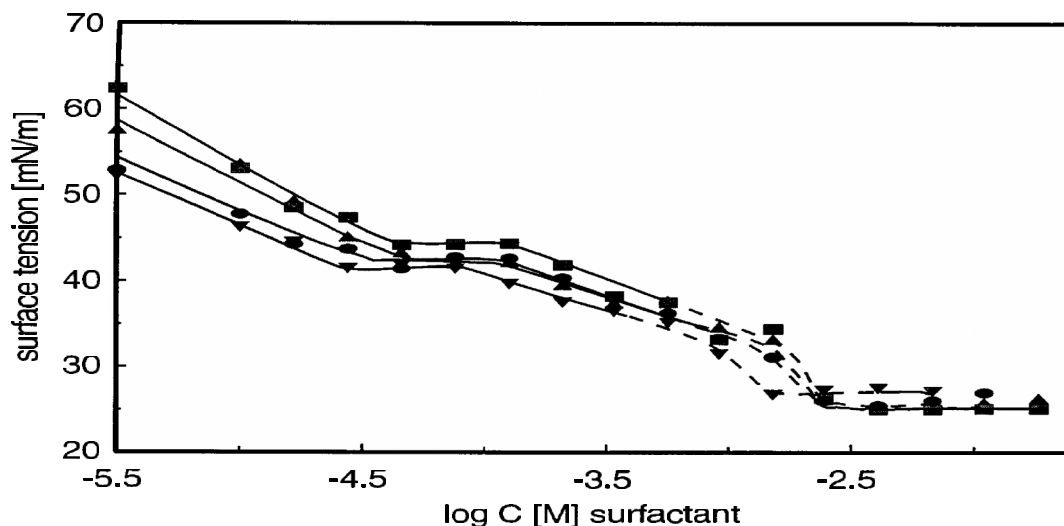


**Fig. 3. Surface tensions of solutions of potato starch (0.01 wt.%, DS=0.80) and SDS/CTAB mixture. The molar ratios of the surfactants were 1:1 (●), 3:1 (✕), 1:0 (▼), 1:3 (▲) and 1:5 (♦).The two-phase domain is indicated by the dotted line**

**Fig. 4. Surface tension of solutions of potato starch (0.01 wt.%, DS=0.80) and NaOct/second surfactant mixtures. The surfactants were NaOct (●), NaOct/CTAB (▼), NaOct/SDS (♦) and NaOct/Tween 20 (▲). The molar ratio of the surfactants in the surfactant mixture was 1:1. The two-phase domain is indicated by the dotted line**

## 3.3. H-bond Formation of Starch with Surfactant

From Figs. 5, it can be seen that starch molecule have many hydroxyl groups and hydrogen atoms which may bind with ionic surfactant molecule through H-atom called intermolecular H-bond. So breakdown of these bonds are easily occurred in hydrophilic and/or hydrophobic parts of surfactant molecule. Hence, cleansing activity increased by the addition of starch in ionic surfactants (SDS, CTAB) (Figs. 6 and 7). Again, the non-ionic surfactants are unable to make H-bond formation with starch molecule (Fig. 8).It is clearly indicated that starch has obviously the property of cleansing activity when it is used nicely as soap or detergent filler in soap-detergent industry.
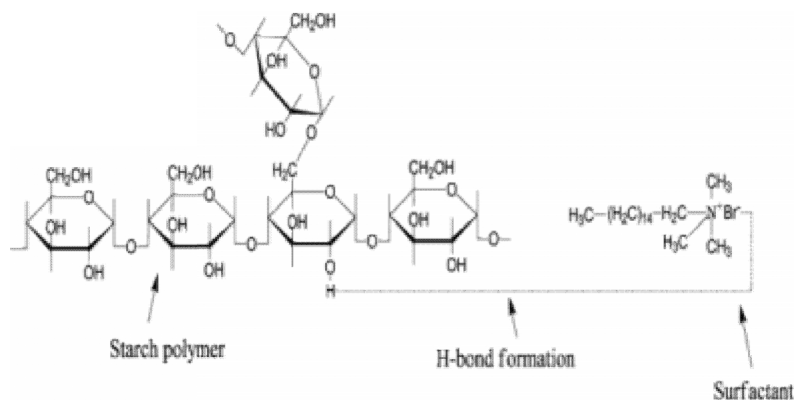


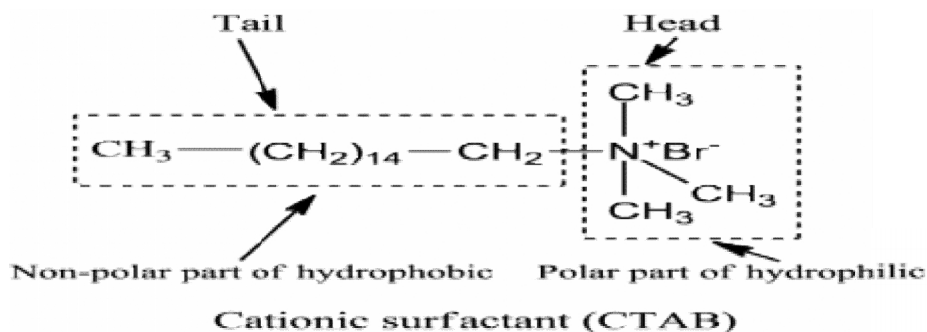**Fig. 5. H-Bond formation of starch with molecule cationic surfactants**

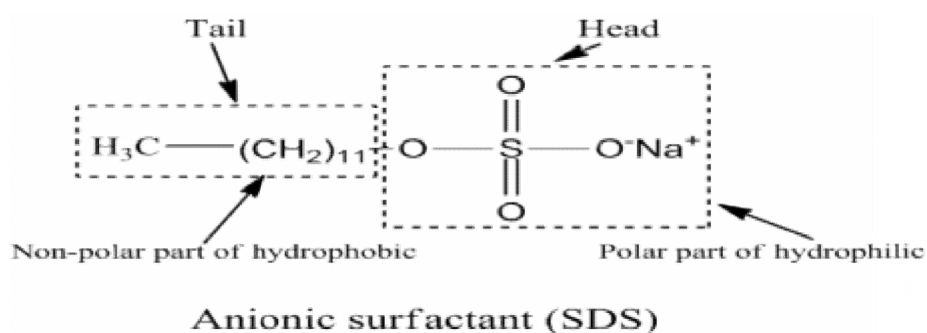**Fig. 6. Cationicsurfactantmolecule**
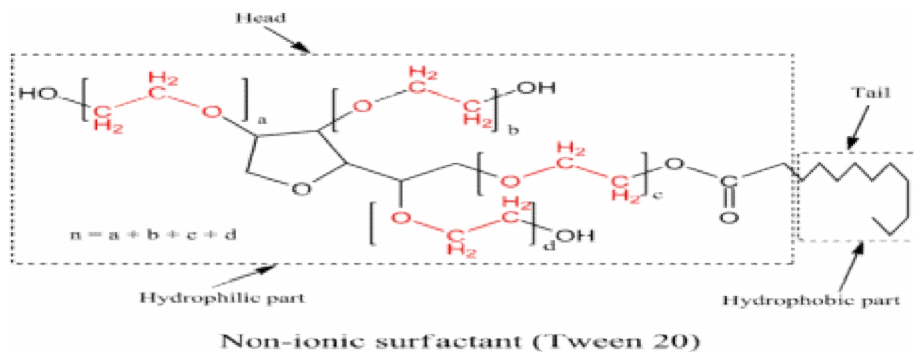


**Fig. 7. Anionic surfactant molecule**



**Fig. 8. Non-surfactant molecule**

## 3.4 Scanning Electron Microscopy (SEM)

Figs. 9 (a-e) show the surface images of starch, SDS, starch-SDS mixture, CTAB and starch-CTAB mixture respectively studied by SEM. It can be seen from Figs. 9(a-e) that the surface images of the starch and surfactant are quite different from each other. The surface images of the starch, SDS and mixture of these two look like granules, pop-corn and needle like respectively. Similar effect was observed in the case of other surfactants. So, it is clear that at a certain temperature and concentration, the starch interacts with the surfactants through the formation of H-bonds and changes its surface structure.

(a) Starch


(b) SDS


(c) Starch with SDS mixture


(d) CTAB


(e) Starch with CTAB mixture
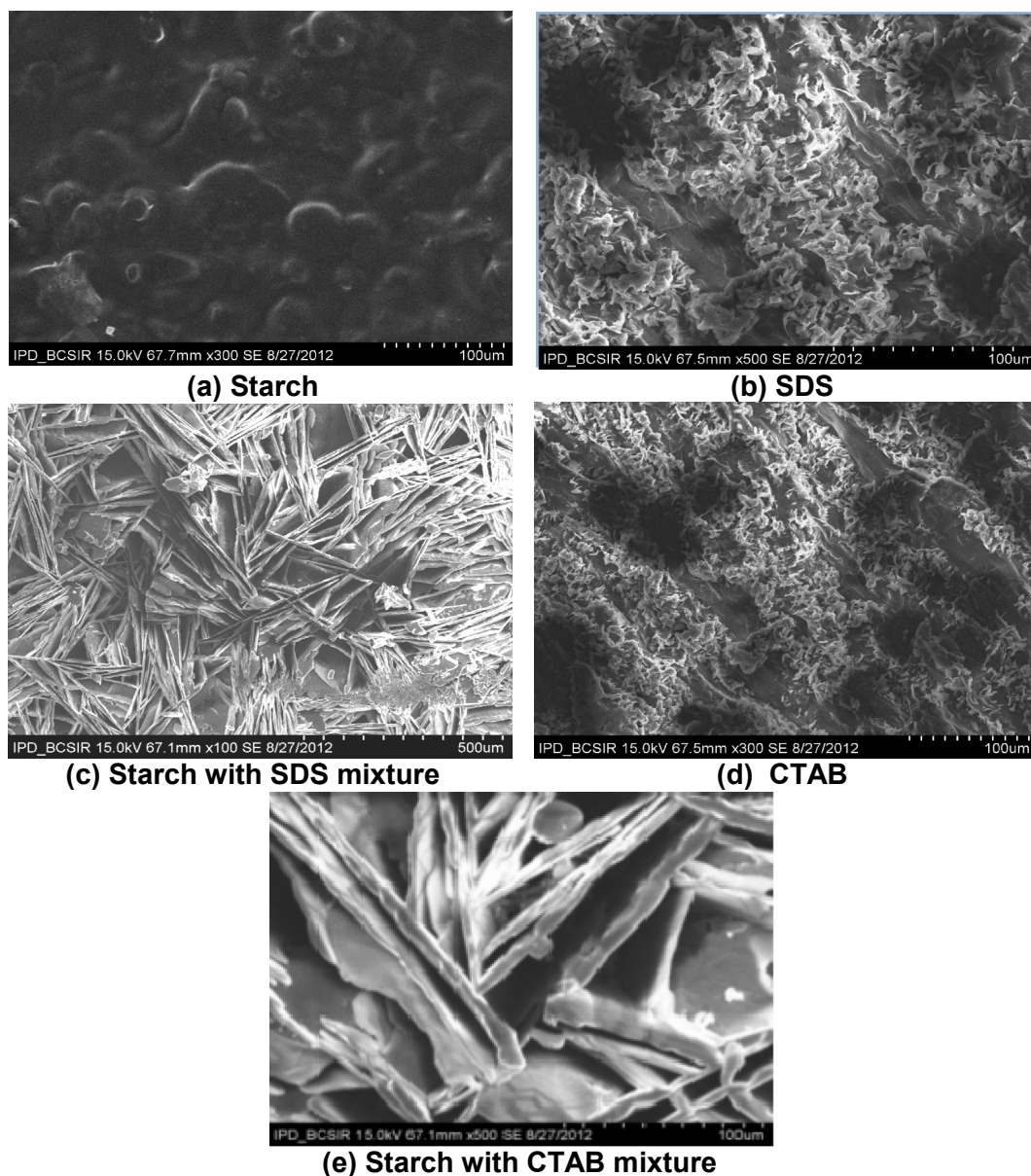
**Fig. 9. SEM images of (a) starch, (b) SDS (surfactant), and (c) starch with SDS mixture, (d) CTAB (surfactant) and (e) starch with CTAB mixture**

## 3.5 FTIR Spectroscopy

It is always difficult to visualize the fundamental mode of vibrations of polymeric molecules. Hydroxyl groups show stretching (along the chemical bonds) and bending or deformation (at right angles to the chemical bonds) modes those give rise to absorption in approx ranges 3600-3100 and 1500-600cm$^{-1}$ respectively. All molecules possessing the hydroxyl group will show such peaks; the exact position of the absorption peaks will vary with the local

environment of the group. Detailed assignments for the peaks observed in spectra of starch and surfactant complexes show a sharp peak at around 3400cm$^{-1}$ for hydroxyl group. In case of non-ionic surfactant (Tween 20). Fig. 10(c) does not show any sharp peak for hydroxyl group whereas a comparative sharp absorption peak is observed in Figs. 10a and 10b. Both CTAB and SDS are ionic surfactants and interact with starch due to which starch molecule form inclusion complexes with them by H atom.

From the IR spectra of Figs. 10(a-c), the following peaks are recognized:

i. At 3400 cm$^{-1}$, -OH vibration in C-OH group;
ii. At 1640 cm$^{-1}$, C=O stretching in –C-OH group;
iii. At 1375 cm$^{-1}$, -O-H in plane deformation in secondary alcoholic group;
iv. At 3650 cm$^{-1}$, N-H vibration in C-OH-N group;
v. IR absorption spectra confirms the complexes in between starch and ionic surfactants (CTAB and SDS). To bind each other by the H-atom to form inter molecular H-bonding with the help of dipolar moment partially positive and negative charges required. Figs. 5 and 6 are shown above mentioned bonding but starch and Tween 20 do not form any H-bonding due to lack of partial positive and negative charges in non ionic Tween 20 surfactant.

The influence of ionic surfactant concentrations on properties of starch based films was analyzed by FTIR spectra. The FTIR spectra of a starch film (without surfactant) is shown in Figs. 10(a) and 10(b). A broad absorption peak at 3268 cm$^{-1}$ is evident due to the stretching frequency of the-OH group, and a peak at 2920 cm$^{-1}$ attributable to C-H stretching vibration [23]. The presence of a strong absorption peak at 1648 cm$^{-1}$ confirms the presence of absorbed water in surfactant. The peaks around 1413 and 1337 cm$^{-1}$ are assigned to -CH$_2$ bending in plane and C-OH bending vibration, respectively. The peak at 1149 cm$^{-1}$ is due to C-O-C anti-symmetric bridge stretching [24]. The FTIR spectra of a CTAB film is shown in Fig.10b. The broad absorption peak at 3260 cm$^{-1}$ is due to the stretching frequency of the–N-H group [25] which overlaps the-OH stretching region at 3480-3440 cm$^{-1}$. The peak at 2876 cm$^{-1}$ is due to the C-H stretching vibration. The peaks around 1412 and 1319 cm$^{-1}$ are assigned to –CH$_2$ scissoring and –OH bending vibration, respectively. The peak at 1060 cm$^{-1}$ is due to CH-O-CH$_2$ stretching [23]. Spectra of CMC films showed peaks around 1592 cm$^{-1}$, attributable to anti-symmetric vibration of COO-groups [26-28]. Addition of ionic surfactant (SDS, CTAB) concentrations to starch films resulted in similar characteristics in the FTIR spectra of Figs. 10(a) and 10(b). This indicated that the anti-symmetric and symmetric vibrations of C=O and C-O bonds were enhanced, probably due to the disruption of intermolecular H-bonds between polar group present in SDS and CTAB molecules caused by added starch [26]. The symmetric COO-stretching was found at~1411 cm$^{-1}$ in all film samples. The water absorption peak of cassava starch at 1648 cm$^{-1}$ disappeared upon addition of CMC. The broad peak located around 3270 cm$^{-1}$ appeared in all films and was caused by O-H stretching and intermolecular/ intra-molecular hydrogen bonds [26]. The N-H peak of CTAB and starch occurred at 3267 and 3261 cm$^{-1}$, respectively. By blending starch with CTAB, the O-H peak of films shifted to 3265-3272 cm$^{-1}$. The peak of C-OH bending of starch film that appeared at 1337 cm$^{-1}$ was shifted to 1322-1333 cm$^{-1}$ peak with SDS addition. Xu et al. [28] reported that the ester bonds were mostly formed between the hydroxyl groups in amylopectin branches of starch and diazonium salt group of CTAB, forming a stable cross-linked structure. This is likely what occurred in the composite starch–ionic surfactant complexes film studied here. These results were correlated with FTIR spectra of rice flour - CMC blended film [29], chitosan-cassava starch-gelatin films [30], and corn starch-CMC-nanoclay bio-composite films [31].
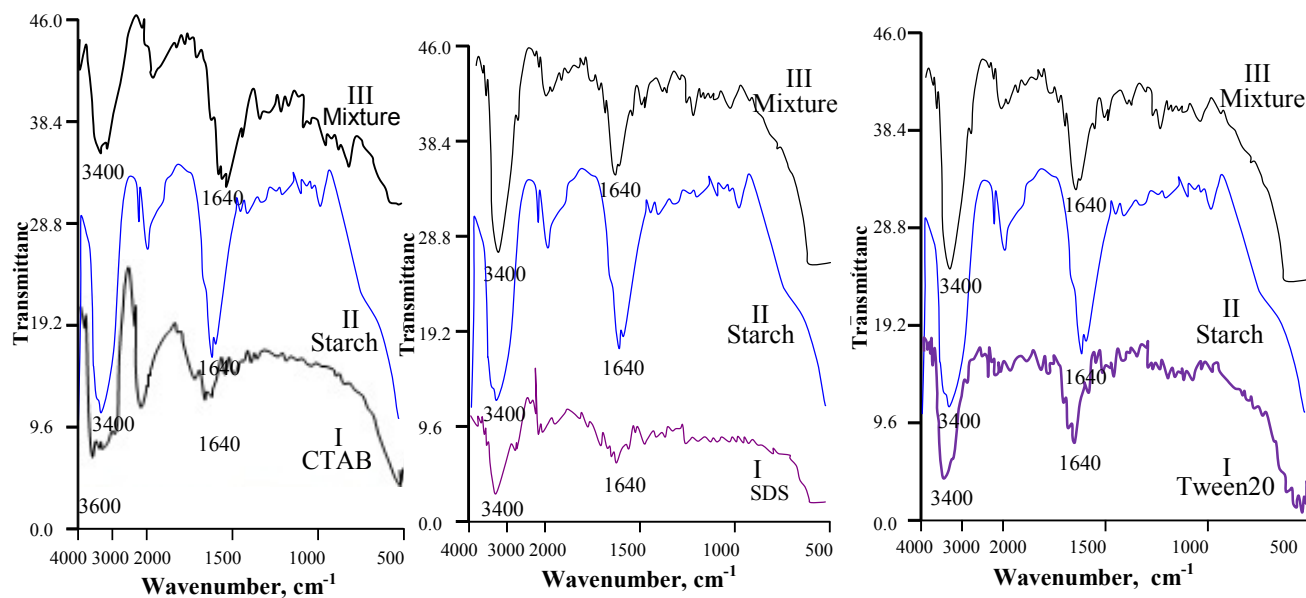
**Fig. 10(a). FTIR Spectra of  I: Cationic (CTAB) surfactant, II: Starch and III: Their mixture**

**Fig. 10(b). FTIR Spectra of I: Anionic (SDS) surfactant, II: Starch and III:    their mixture**

**Fig. 10(c). FTIR Spectra of I: Non-ionic (Tween 20) surfactant, II: Starch and III: Their mixture**

## 4. CONCLUSION

The investigations presented in this paper show that strong ionic interaction occurs between cationic and anionic surfactants (CTAB, SDS) except non-ionic surfactant (Tween 20) and starch polymer, leads to phase separation and precipitation of the formed amorphous complexes. Complex formation on starch depends on the chain length difference in exactly in the same way as for free mixed micelles. The separated complex phase is a hydrophobic, highly viscous and gel like containing 40 to 60% water. The high and low water content of the complex phase indicates that the interactions between the starch and ionic surfactants are very strong and they are capable more effective cleansing than normal detergent available our indoor market but also biodegradable and eco-friendly for environment. The ionic surfactants (CTAB, SDS) at concentrations above its critical micelle concentration reduces the inter-polymer association through micelles formation around hydrophobic (alkyl group) groups. The presence of a miscible starch molecule also reduces inter-polymer association by preferential salvation of the hydrophobic groups.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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