

Study of Starch Based Biodegradable Polymeric Surfactants for Better Cleansing Activity

ABSTRACT

In the present case, biodegradable starch interactions with various surfactants has been studied for the investigation of ability and cleansing activity of starch-surfactant-water system. The surfactants investigated were sodium dodecylsulphate(SDS), sodium octanoate(NaOct),cetyltrimethylammoniumbromide(CTAB) and tween-20. The 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 volume difference between the hydrocarbon chains length. Mixed micelle formation with starch depends on the chain-length 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 with 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 and it showed maximum cleansing activity of respective detergent. From the experimental results of viscosity, surface tension and other physical properties it indicated that adding starch in detergent as soap filler these properties have changed. The complexes were analyzed and characterized by FTIR, XRD and SEM. Some of the complexes exhibited excellent emulsifying efficiency and surfactants performance properties with this biodegradable starch polymer.

Key words:Starch, surfactants, cleansing activity, surface tension, starch-surfactant complex

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

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32 potentially very interesting substitutes for non-biodegradable petroleum-based polymers.
33 An attractive field of application of these polymers is their use as packaging materials. For the current
34 petrochemical-based products recycling is often neither practical nor economically feasible
35 [1]. Natural polymers such as starch, cellulose or proteins are potentially very interesting starting
36 materials for biodegradable packaging materials.

37
38 In particular, starch is an attractive as it is relatively cheap and abundantly available.
39 However, the general picture emerging from these
40 studies is that in dilute solution the surfactant molecules adsorb polymer chains as micellar or
41 micelle-like clusters. A general phenomenon in systems of polyelectrolyte and
42 oppositely charged surfactant is that complexes of these components separate as a water-
43 swollen phase in equilibrium with very dilute aqueous solution. Generally, the rich
44 phase behavior of surfactants in water is also characteristic of starch-surfactant
45 complexes in contact with water. Thus, in complexes, the interactions may be intra and/or
46 intermolecular. The balance depends on the structural parameter necessary for softening the
47 polymer, such as the nature, lengths and content of hydrophobic groups, their distribution
48 along the starch, the hydration capacity, the degree of polymerization, polymer concentration
49 and on other parameters such as salinity, pH and organic co-solvents [2,3]. Among the
50 associated polymers, amphiphilic polysaccharides with a natural non-toxic and biodegradable
51 carbohydrates are of particular interest. They were prepared by the hydrophobic modification
52 of a variety of polysaccharides, such as corn, potato [4], hydroxyethylcellulose,
53 carboxymethyl cellulose [5,6] and pullulan [7]. Increasing interest has been focused on the
54 structure-solution property relationship of amphiphilic polysaccharides [8-10]. The
55 associative behaviors of hydrophobically modified carboxymethyl cellulose and
56 carboxymethyl pullulan were studied after the amidation of these polysaccharides in DMSO
57 [6,7]. In a previous study, the hydrophobization of various polysaccharides were investigated,
58 such as hydroxyl ethylcellulose [11], carboxymethyl cellulose [12], xylan [13], and
59 carboxymethyl starch [14,15] by the esterification of hydroxyl groups using classical (with
60 acyl chloride and mixed anhydride) and unconventional methods. The interactions of
61 surfactants with cationised cellulose, has been studied by Goddard et al. [16,17] and

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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 monoglucose 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 depicted that many researchers have paid their attention on this field. In spite of half century of great effort, many academic aspects such as, chemistry, chemical reactions, bond formation on 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 surfactants complexes studied by the ternary phase diagram, interfacial surface tension and viscometric measurement. The instruments like XRD, SEM, FT-IR etc. were used to characterized the product samples in these investigations.

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2. MTERIALS AND METHODS

2.1 Materials

Starch was purchased from UNI-CHEM, China and its degree of substitution (DS) was 0.80 starch solution was prepared by heating in water in an autoclave at 120°C for 30 min. All solutions were prepared at least 24h before measurements were performed. The surfactants

sodium dodecylsulphate(SDS), N-cetyl-N,N,N-trimethylammoniumbromide(CTAB), sodium octanoate(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 $71.5 \times 10^{-3} \pm 0.5$ N/m at 30°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. The reproducibility results between measurements of the same sample was ± 0.5 N/m. The results of the surface tension measurement were calculated from the equation below:

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

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 γ 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 $\pm 0.1^\circ\text{C}$ was used. The flow of time was recorded by a timer accurate up to ± 0.01 second. At certain surfactant/starch ratios 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

122 calculated from equation below:

123
$$\eta_{red} = \frac{(t - t_0)}{C}$$

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

126

127 2.2.3 SEM analysis

128 Scanning Electron Microscope (SEM) of potato starch, surfactant and starch-surfactant
129 complexes were less than 4% moisture content before examined. Dried sample were taken onto
130 the double-sided adhesive tape attached to the specimens tub. The excess sample was removed
131 and the sample was placed in fine coater of gold coating for 150 sec. The coated sample was
132 then placed in the sample chamber of the SEM. The sample was examined at a magnification of
133 2,500 and 6,000 with the accelerating voltage of 10 kV.

134

135 2.2.4 FTIR spectroscopic analysis

136 Potato starch is a polymer, cetyltrimethylammonium bromide (CTAB) is a cationic surfactant
137 and sodium dodecyl sulphate (SDS) is a anionic surfactant. About 0.2 g sample was dried in an
138 electric oven at 105°C for 30 min. Tween-20 is a non-ionic highly viscous liquid. About 10ml
139 sample was taken into glass tray and dried at 105°C for 2h. Samples with KBr was ground with a
140 mortar-pastle and a pellet was made. FTIR of the KBr pellet was measured with Shimadzu
141 FTIR-470 infra-red spectrophotometer between 400 - 4000 cm⁻¹.

142

143 3. RESULTS AND DISCUSSION

144 3.1 Surface active properties

145 Some of the prepared starch-surfactant mixture lowered the surface tension of water, namely at
146 lower concentration of the sample Table 1. The functional properties of some of the prepared You
147 have generally not discussed effect of all the surfactants. Please do discuss them surfactant and
148 starch mixed surfactant solutions were tested for emulsifying efficiency, washing power and anti-
149 redeposit efficiency. The emulsifying efficiency was characterized by the stability of the
150 paraffinic Tween-20/water emulsions and other surfactant mixture at definite ratio. The results
151 summarized in Table 2 shows that some of the surfactant made emulsions of the oil/ water type

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stable even after 24h. Starch mixed ionic surfactant cleansing efficiency was comparable to that of the commercial emulsifier Tween-20. Some of the tested mixture showed excellent washing power exceeding that of the anionic detergent, name 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].

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3.2 Analysis by viscometric measurement

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 concentrations of binary surfactant mixture 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	-

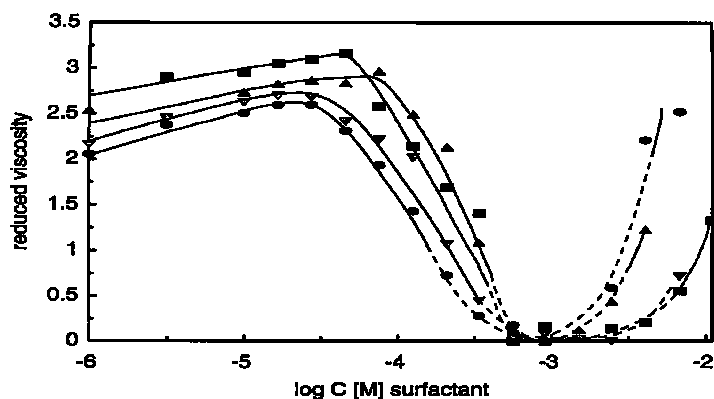


Fig. 1 Reduced viscosities of solutions of potato starch (0.01 wt.%, $DS=0.80$) and NaOct/second surfactant mixtures. The surfactants were NaOct(●), NaOct/CTAB (▼), NaOct/SDS (◆) and NaOct/Tween-20 (▲). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The two-phase domain is indicated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

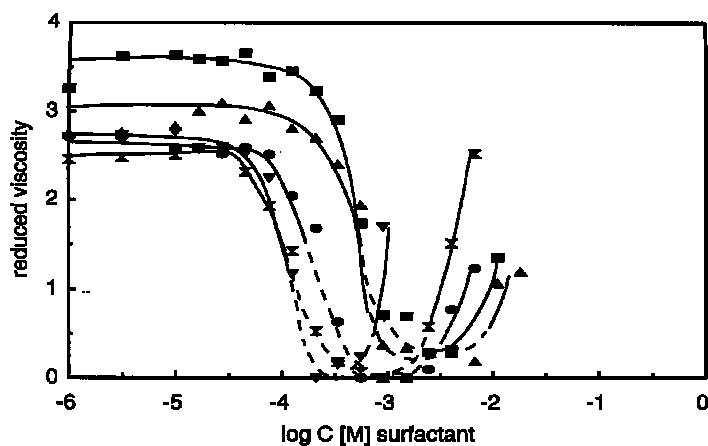
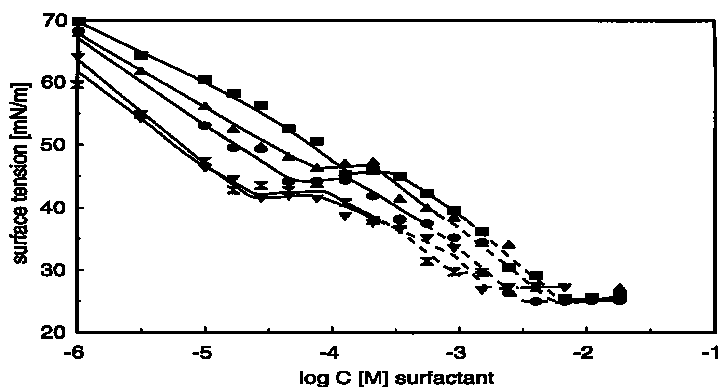


Fig. 2 Reduced viscosities of solutions of starch (0.01 wt %, $DS=0.80$) and SDS/CTAB mixtures. The molar ratios of the surfactants were 1:0 (▼), 3:1 (⊗), 1:1 (●), 1:3 (▲) and 1:5 (◆). The two-phase domain is indicated by the dotted line.



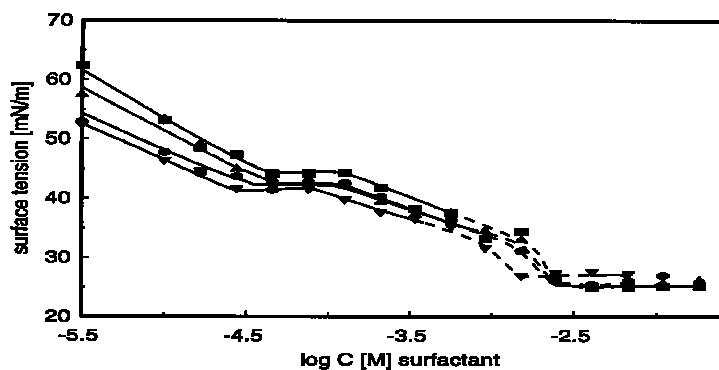
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171 Fig. 3 Surface tensions of solutions of potato starch (0.01 wt.%, DS=0.80) and SDS/CTAB
 172 mixture. The molar ratios of the surfactants were 1:1 (●), 3:1(⊗), 1:0 (▼), 1:3(▲)
 173 and 1:5 (◆).The two-phase domain is indicated by the dotted line.

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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 was1:1.The two-phase domain is indicated by the dotted line.

Fig.1 shows the reduced viscosity of starch solutions containing different surfactant mixtures. The viscosity drop occurs at lower concentrations as the hydrocarbon chain length of the second surfactant is increased. Thus, the interaction depends markedly on the surface activities of the surfactants. The viscosity increase 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 concentration at which the sudden viscosity reduction occurred and increased, when the NaOct/CTAB molar ratio is 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 fixed starch concentration but variable surfactants concentration, it has been found that at certain concentration of surfactant surface tension value is minimum which indicated maximum cleansing activity appeared at the mentioned points. **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. **Figure 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 slopes of the curves. When part of the NaOct is replaced by CTAB, the CMC (critical micelle concentration) increases with an increase in mole fraction of the short-chain surfactant. At concentrations considerably above those values corresponds to charge equivalence between the amounts of surfactant and starch, a complex phase containing high concentration 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 $\text{NaOct} < \text{CTAB} < \text{SDS} < \text{Tween20}$. Redissolution, which is not complete with this highly charged starch ($\text{DS}=0.80$), 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 not only this, the product is biodegradable hence it is also eco-friendly.

3.3. H-bond formation with surfactant

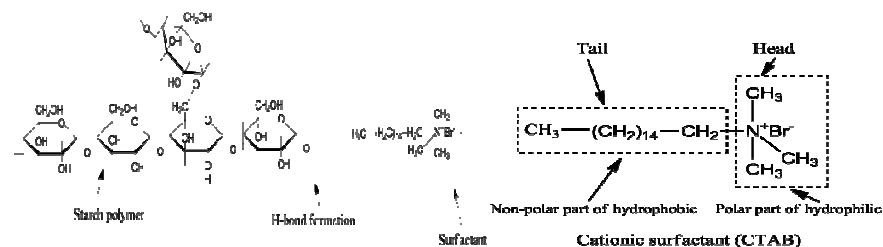


Fig. 5 H-Bond formation starch with cationic surfactants.

Fig. 6 Only cationic surfactant molecule.

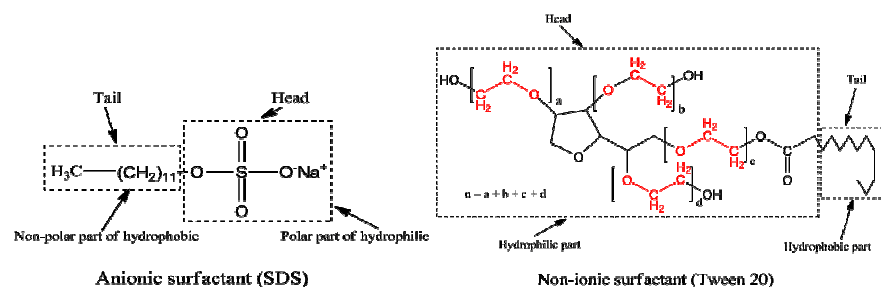


Fig. 7 Only anionic surfactant molecule. **Fig. 8** Only Non- surfactant molecule.

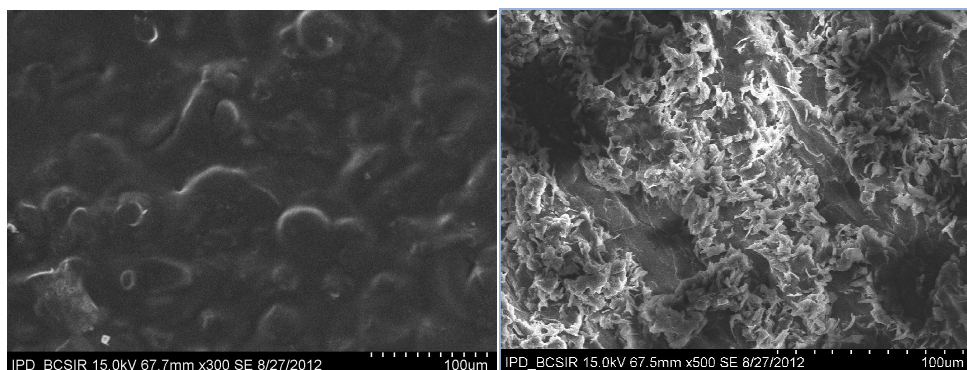
From **Figs. 5 and 6**, it can be seen that starch molecule have many hydroxyl groups and hydrogen atoms which may bind with ionic surfactant molecule through H-atom called intermolecular H-bond. So breakdown of these bonds are easily occurred in hydrophilic and/or hydrophobic parts of surfactant molecule. Hence, cleansing activity increased by adding starch in ionic

surfactants(SDS,CTAB. Again, the non-ionic surfactants are unable to make H-bond formation withstarch molecule.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.

3.4 ScanningElectronMicroscopy(SEM)

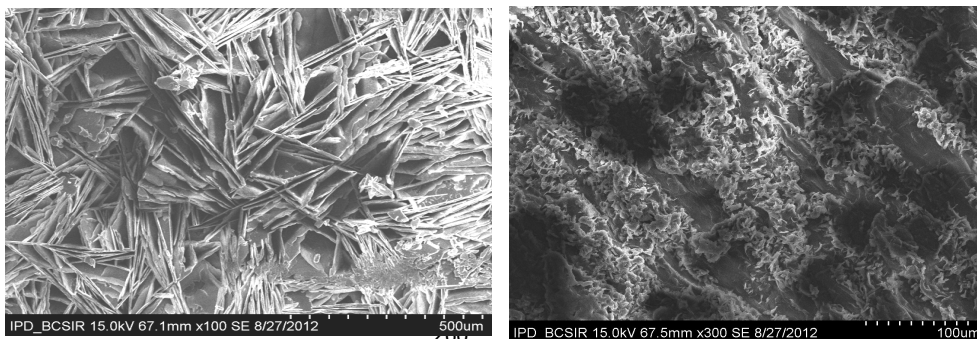
Figs. 7a,b, c, d and e show the individual surface image of starch, SDS, starch-SDS mixture, CTAB and starch-CTAB mixture respectively studied by SEM.It can be seen from **Figs. 7a, b c, d and e** that the surface images of the starch and surfactant are quite different from each other. The surfaces of the starch, **SDS and** mixture of these two looks likegranules, 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, thestarch interacts with the surfactants through the formation of H-bonds and changes its surface structure.

Comment [E8]: What of images of CTAB, NaOct and Tween20, more one surfactant image was included and sufficient for understanding.



a. Starch

b. SDS



c. Starch with SDS mixture

d. CTAB



(e) Starch with CTAB mixture

Fig. 7 SEM image 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 that give rise to absorption in approx ranges 3600-3100 and 1500-600 cm^{-1} respectively. All molecules possessing the hydroxyl group will show such bands; the exact position of the absorption bands will vary with the local environment of the group. Detailed assignments for the bands 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. 8c** does not show any sharp peak for hydroxyl group whereas a comparative sharp absorption peak is observed in **Figs. 8a and 8b**. Both CTAB and SDS are ionic surfactants and interact with starch due to which starch molecule form inclusion complexes with them by H atom.

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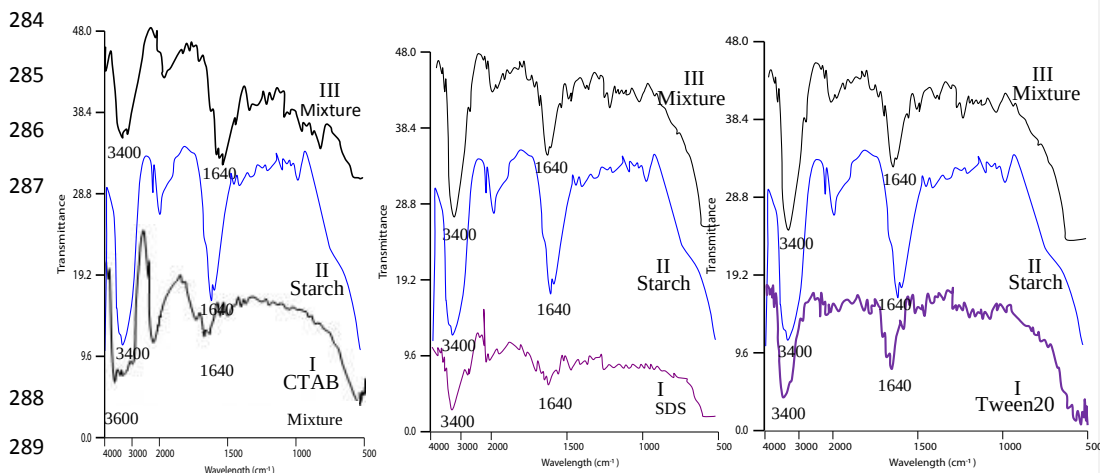


Fig.8(a) FTIR Spectra of I: Cationic (CTAB) surfactant, II: Starch and III: Their mixture

Fig.8(b) FTIR Spectra of I: Anionic (SDS) surfactant, II: Starch and III: Their mixture

Fig.8(c) FTIR Spectra of I: Non-ionic (Tween-20) surfactant, II: Starch and III: Their mixture

From the IR spectra of **Figs. 8.a, b and c**, the following peaks are recognized:

- At 3400 cm^{-1} , -OH vibration in C-OH group;
- At 1640 cm^{-1} , C=O stretching in -C-OH group;
- At 1375 cm^{-1} , -O-H in plane deformation in secondary alcoholic group;
- At 3650 cm^{-1} , N-H vibration in C-OH-N group;
- 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 charge required. Figure 5 and 6 are shown above mention bonding but starch and Tween-20 do not form any H-bonding due to lack of partial positive and negative charge in non ionic Tween-20 surfactant.

The influence of ionic surfactant concentrations on properties of starch based films was analyzed by FTIR spectra. **mechanical properties of the films, water solubility, and film morphology as reported below.**

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308 All the starch films with and without surfactant appeared smooth, clear, and
 309 transparent. Film thickness was ranged from 120 to 160 μm . The FTIR spectrum of a starch film
 310 (without surfactant) is shown in **Figs. 8a and 8b**. A broad absorption band at 3268 cm^{-1} is
 311 evident, due to the stretching frequency of the -OH group, and a band at 2920 cm^{-1}
 312 attributable to C-H stretching vibration [23]. The presence of a strong absorption band
 313 at 1648 cm^{-1} confirms the presence of absorbed water in surfactant. The bands around 1413
 314 and 1337 cm^{-1} are assigned to -CH₂ bending in plane and C-OH bending vibration,
 315 respectively. The band at 1149 cm^{-1} is due to C-O-C anti-symmetric bridge stretching [24]. The
 316 FTIR spectrum of a CTAB film is shown in **Fig. 8b**. The broad absorption band at 3260 cm^{-1}
 317 is due to the stretching frequency of the -N-H group [25] which overlaps the -OH stretching
 318 region at 3480-3440 cm^{-1} . The band at 2876 cm^{-1} is due to the C-H stretching vibration. The
 319 bands around 1412 and 1319 cm^{-1} are assigned to -CH₂ scissoring and -OH bending vibration,
 320 respectively. The band at 1060 cm^{-1} is due to CH-O-CH₂ stretching [23]. Spectra of CMC
 321 films showed peaks around 1592 cm^{-1} , attributable to anti-symmetric vibration of COO⁻ groups
 322 [26] and [28]. Adding ionic surfactant (SDS, CTAB) concentrations to starch
 323 films resulted in similar characteristics in the FTIR spectra (**Figs. 8a and 8b**). This indicated
 324 that the anti-symmetric and symmetric vibrations of C=O and C-O bonds were enhanced,
 325 probably due to the disruption of intermolecular H-bonds between polar group present in SDS
 326 and CTAB molecule caused by added starch [26]. The symmetric COO⁻
 327 stretching was found at ~1411 cm^{-1} in all film samples. The water absorption band of cassava
 328 starch at 1648 cm^{-1} disappeared upon addition of CMC. The broadband located around
 329 3270 cm^{-1} appeared in all films and was caused by O-H stretching and intermolecular/ intra-
 330 molecular hydrogen bonds [26]. The N-H band of CTAB and starch occurred at
 331 3267 and 3261 cm^{-1} , respectively. By blending starch with CTAB, the O-H band of films shifted
 332 to 3265-3272 cm^{-1} . The band of C-OH bending of starch film that appeared at 1337 cm^{-1} was
 333 shifted to 1322-1333 cm^{-1} with SDS addition. Xu et al. [28] reported that the ester bonds were
 334 mostly formed between the hydroxyl groups in amylopectin branches of starch and
 335 diazonium salt group of CTAB, forming a stable cross-linked structure. This is likely what
 336 occurred in the composite starch-ionic surfactant complexes film studied here. These results

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Comment [E18]: This can only be measured within the OH band. Don't forget the structure of starch : Disruption of H-bond occurred between starch and ionic Surfactant (SDS, CTAB).

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Ok as the range mentioned.

337 were correlated with FT-IR spectra of rice flour -CMC blended film [29], chitosan-cassava
338 starch-gelatin films [30], and corn starch-CMC-nanoclay bio-composite films [31].

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340 4. CONCLUSION

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

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