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Eco-Friendly Biodegradable Semi-Natural Surfactants from Starch for Green Chemistry

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Abstract: *The biodegradable starch-polymer interactions with various surfactants, such as sodium dodecyl sulphate, sodium octanoate, cetyltrimethyl ammonium bromide and Triton-X-100, were investigated. The goal was to produce eco-friendly biodegradable semi-natural surfactants. Yet they also had to be capable of cleansing dirty particles and of washing dishes. Thus, the goal was "cleanliness through green chemistry". The DS of starch and its concentrations used were 0.8 and 0.01 to 1% wt/v, respectively. The effect of mixing on the micellization of the ternary surfactant solutions can be estimated by measuring only the effects of the difference between the lengths of the hydrocarbon chains. Formation of mixed micelle 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 starch 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 active component is strongly enriched in the polymer complexes of gels. It showed maximum cleansing activity of the respective surfactants. From the experimental results of viscosity, surface tension and other physical properties, it indicated that adding starch in surfactant as soap filler has changed these properties. The complexes obtained from the ternary phase were analyzed and characterized by FTIR spectroscopy, XRD and SEM. Some of the prepared complexes exhibited excellent emulsifying efficiency and surfactant performance properties. Thus, the prepared semi-natural surfactants from potato starch are safe for water and for animals. The goal of green chemistry, which does not add to global warming or harm the natural environment, was met. Use of such surfactants can reduce the use of chemical soap or detergents for cleansing, which can have negative effects on the environment and on human and animal health.*

Keywords: *Starch, Surfactants, Cleansing activity, Ternary phase diagram, Green chemistry*

I. Introduction

Starch, a naturally-occurring, high-molecular-weight polymer of α-D-glucose, consists of two main fractions: amylose and amylopectin. Amylose and amylopectin possess different properties and are therefore best suited for different applications [1]. The amylose molecule is capable of forming helical inclusion complexes with a variety of organic substrates [2].

The fundamental property of a surfactant is its ability to form aggregates in solution, or "micelles". Micelles are formed at low surfactant concentrations in water. The concentration at which micelles start to form is called the "critical micelle concentration".

The anionic surfactants carry a negatively-charged head group. The cationic surfactants carry a positively-charged head group. The non-ionic surfactants have no charge on their head groups [3].

The cleansing activity of a surfactant is one of the most important cleansing tools in daily life. Thus, the improvement of cleansing activity and biodegradability of a soap or detergent is obviously required for better quality and performance. Green, biodegradable polymers, derived from natural resources, such as rice, potato, corn starch etc. are potentially very interesting substitutes for non-biodegradable petroleum-based polymers.

An attractive field of application for these polymers is their use as packaging materials, especially for food packaging. For the current petrochemical based-products, recycling is often neither practical nor economically feasible [4]. Indeed, in most cases these are hazardous. Natural polymers such as starch, cellulose or proteins are potentially very interesting starting materials for biodegradable packaging materials.

In particular, potato starch is attractive, as it is relatively cheap and abundantly available in any south Asian country like Bangladesh, India or Pakistan. However, the use of native starch for packaging materials is limited due to its low moisture resistance, poor processibility (high viscosity), high brittleness, and incompatibility with hydrophobic polymers.

Hence, modification of potato starch is therefore required, to introduce hydrophobicity and to improve mechanical and moisture barrier properties. Thus, the interactions may be intra- and/or inter-molecular. The balance depends on the structural size and nature of the polymer: the nature, lengths and content of hydrophobic groups; their distribution along the starch; their hydration capacity; the degree of polymerization; polymer concentration; and on other parameters, such as strength, salinity, pH and organic co-solvent [5,6].

Among the polymers, amphiphilic starch, with 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 [7], hydroxyethylcellulose, carboxymethyl cellulose [8,9] and pullulan [10].

Increasing interest has been focused on the structure-solution property relationship of amphiphilic polysaccharides [11-13]. The associative behaviors of hydrophobically modified carboxymethyl cellulose and carboxymethyl pollulan were studied after the amidation of these polysaccharides in DMSO [9,10]. Some authors investigated the hydrophobization of various polysaccharides, such as hydroxyl ethylcellulose [14], carboxymethyl cellulose [15], xylan [16], and carboxymethylstarch [17,18]. These studies carried out esterification of hydroxyl groups, using classical (with acylchloride and mixed anhydride) and unconventional methods. The interaction of surfactants with cationized cellulose has been studied by Goddard et al. [19,20] Non-ionic cellulose ethers have been subject of extensive studies by Piculell and Lindman [21].

The structure and characteristics of starch are very similar to cellulose, but the difference in the bindings, which link the monoglucose units to form the polymer, makes their chemical behaviors 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 chains, having intra- and inter-molecular hydrogen bondings. Thus, actually, starch is a very different material to cellulose despite of their chemical similarities.

The infrared *spectra* of starch and related compounds have been studied for a long time by a number of authors [22,23]). These authors investigated the chemical changes in starch, the effect of hydrogen bonding and change in the crystalline structure of starch. Starch-surfactants complex interactions of H-atoms of starch, within the surfactant molecule, by the H-bonding process are now subject to IR absorption of the functional groups. This may vary over a wide range.

From the above summary, it appears that many researchers have given their attention to this field. In spite of a half-century of great effort, many academic aspects, such as, chemistry, chemical reactions and bond formation on starch-surfactants interaction are still open for further research.

The purpose of the present investigation is to explore the effect of potato starch interaction with various surfactants (ionic and non-ionic). Further, the study will seek to find better reaction mechanisms and to understand the real interaction of potato starch and surfactant complexes. Methods will include the ternary phase diagram, interfacial surface tension, reduced viscosity measurement and XRD, SEM and FT-IR instrumental analysis.

II. Experimental

2.1 Materials

Starch was purchased from UNI-CHEM, China: its degree of substitution (DS) was 0.80. Starch solution was prepared by heating the starch, in water, in an autoclave, at 120°C for 30 minutes. All solutions were prepared at least 24 hours before measurements were performed. The ionic surfactants, such as sodium dodecyl sulphate (SDS), N-cetyl- N,N,N-trimethyl ammonium bromide (CTAB) and sodium octanoite (NaOct), were purchased from Loba Chemicals Ltd., India. Triton X-100 (polyoxyethlene isooctylphenol), as a non-ionic surfactant, was purchased from BDH Chemicals Ltd., England.

All these chemicals used were analytical grade, and were used without further purification. The starch solution's conductivity and reduced viscosity were 2.0 µs and 4.0 dm^3/mol, respectively, and its surface tension was $71.5\times10^{-3} \pm 0.5$ N/m at 30°C.

2.2 Methods

2.2.1 Ternary Phase Diagram

For the development of ternary phase diagrams, the formulated samples were taken into the test tube by varying their compositions in such a way that the total composition remained 100%. The samples in each test tube were prepared by varying 5% composition of two components simultaneously, keeping the third component constant, and transferring them to alternative test tubes.

The test tubes were then shaken, for effective mixing of the components, and placed into the diagram according to the composition and mark. After completion of the 228 samples, according to the diagram, on the wooden frame, the open end of the test tube was then closed tightly with cork. This procedure assures that there will be no leakage and that the lower part of the cork did not touch the sample solution. These samples were then left to equilibrate in a thermostat box, at 30°C, for at least ten days. During this period of equilibration, they were shaken from time to time. The equilibrium was established within this period [28].

2.2.2 Viscosity

Viscosities were determined with an Ostwald viscometer, according to British standard (Fisher Scientific TM 200). The flow of time was recorded by a timer, accurate up to ± 0.01 seconds. At certain surfactant/starch ratios, the aggregates formed were very mobile flocks. This could be avoided partly by draining the capillaries fully between measurements. The results of the viscosity values were calculated using the equations below:

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

where, t is the measured efflux time of solutions and t_0 is the efflux time of the water, c is the concentration of the surfactant, starch and surfactants-mixed polymer.

2.2.3 SEM analysis

Scanning Electron Microscope (SEM) scans of potato starch, surfactant and starch-surfactant complexes were examined. Dried samples were taken onto the double-sided adhesive tape attached to the specimen's tub. The excess sample was removed and the sample was placed in a fine coater of gold coating for 150 seconds. The coated sample was then placed in the sample chamber, and was examined at a magnification of 2,500 and 6,000, with an accelerating voltage of 10 kV.

2.2.4 FTIR spectroscopy

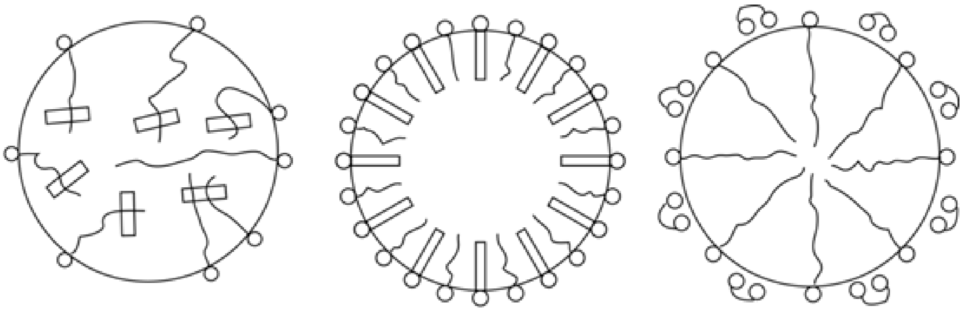
Potato starch is a natural, biodegradable polymer. Cetyltrimethyl ammonium bromide is a cationic surfactant. Sodium dodecyl sulphate is an anionic surfactant.2g sample was dried at 105°C for 30 minutes. Triton-X-100, a high-viscous non-ionic liquid surfactant was used. A 10 ml sample was taken into a glass tray and dried at 105°C for 2 hours. A sample with KBr was then ground with a mortar-pastle, to make a pellate. The FTIR of the KBr pellate was measured with a Shimadu FTIR-470 infra-red spectrophotometer (Japan).

III. Results And Discussion

3.1 Solubilization properties of natural surfactant from potato starch

The solubilization begins at critical micelle concentration (CMC), which indicates that the solubilization molecules are taken up by the micelles. Three modes of solubilization have been proposed for ionic surfactants. These are:

1. Incorporation in the hydrocarbon centre of the micelle;
2. Incorporation in to the polished layer of the micelle;
3. Adsorption on the surface of the micelle;



1a Surface active agent

1b Solublizate

1c Micelle in Surface

Fig.1(a-c). Schematic diagram of three modes of solubilization.

When a solution containing non-ionic surfactant is heated gradually, it shows turbidity at a certain level of temperature, which is called the "cloud point". On further heating, the solution becomes separated into two phases: one is enriched in surfactant concentration and the other one is depleted.

The presence of solubilizate and its effect, on both cloud point and the phase separation temperature, due to appropriate crystallinization, have been identified. The direction (increase or decrease) and magnitude of solubilization depend on: (1) the amount of solubilizate and (2) its type.

Thus, in some cases, a progressive addition of solubilizate causes clouding. Before reaching phase separation, the limit of solubilization is normal. In such cases, the phase is separated from the solution, containing a mixture of water and solubilizate. The phase is especially rich in surfactant. When the solubilization limit is overcome, almost pure solubilizate is separated out.

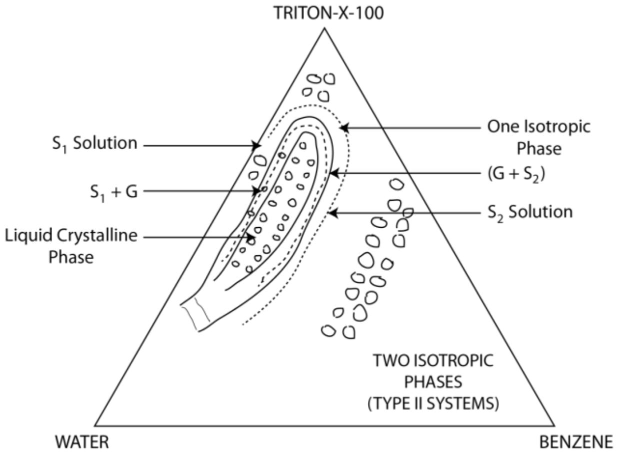


Fig.2. Phase diagram of the Triton X-100 /Benzene /water system.

It is experimentally shown in Fig. 1 and 2 that the micellar weight of a polyoxyethylene type of nonionic surfactant is increased by the elevation of temperature. As the cloud point is approached, the micellar weight will increase [24]. Finally, it comes to a point where the micelle becomes so large that it will be noticeable even to the naked eye.

Further growth will cause the separation of a surfactant-rich phase. This interpretation indicates that the cloud point is accompanied by the formation of giant molecules. After the phase separation has been completed, the concentration of the surfactant is low in the co-existing water-rich phase, because there are no or few micelles present. It is believed that the hydration of other oxygen atoms of the polyoxyethelene group is, generally, the main factor in keeping the non-ionic surfactant in solution. Then, increase in temperature causes partial dehydration and finally results in the separation of the surfactant-rich phase.

Non-ionic surfactants, having longer polyoxyethelene groups, as shown in Fig. 2, have a higher cloud point, by virtue of their greater capacity to hydrate. Yet a recent report by Murata and Arai [25] has thrown doubt on the idea that the increase in temperature decreases hydration.

The discrepancy (at least partially) is due to the different definitions of hydration. The water hydration bond to ether oxygen will decrease with rising temperature, whereas the water trapped in the polyoxyethylene mesh may increase. The cloud point is influenced by the presence of certain additives but insensitive to the surfactant concentration. Certain substances do not depress the cloud point. On the other hand, some other substances depress the cloud point. The depression is moderate in comparison to starch used as a co-builder in detergents [26].

Table1. Critical micelle concentrations of binary surfactant mixture of SDS, CTAB, Triton X-100 and NaOCt.

Mole fraction	SDS/ CTAB	SDS/ Trion X-100	CTAB/Trion X-100	NaOCt/CTAB	NaOCt/Trion X-100	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

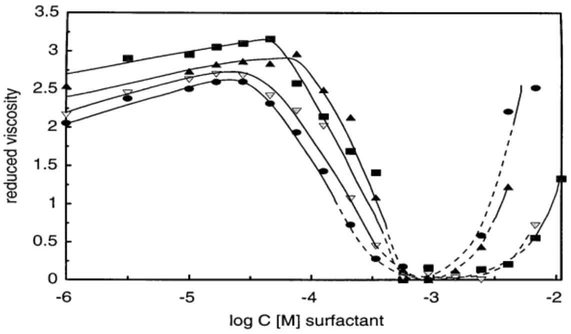


Fig. 3. Reduced viscosities of potato starch solution (0.01 wt. %, DS=0.80) and NaOct/second surfactant mixtures. The surfactants were NaOct (●), NaOct/ CTAB (▼), NaOct/SDS (◆) and NaOct/Trion X-100 (▲). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The dotted line indicates the two-phase domain [27].

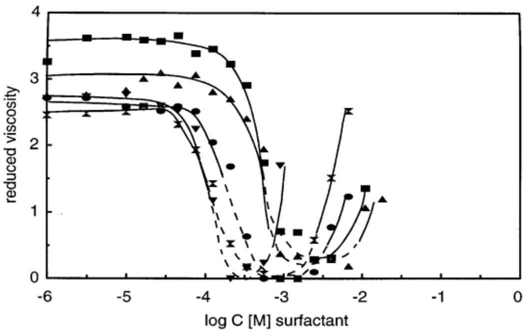


Fig. 4. Reduced viscosities of potato starch solution (0.01 wt. %, DS=0.80) and SDS/CTAB mixture. The molar ratios of the surfactants were 1:0 (▼), 3:1 (⧗), 1:1 (●), 1:3 (▲) and 1:5 (◆). The dotted line indicates the two-phase domain [27].

Figure 3 shows the reduced viscosity of potato 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, it is clear that the interaction depends markedly on the surface activities of the surfactants.

The viscosity increases as excess surfactant begins to dissolve. At the same time, the added excess surfactant starts to form micelles. The result is an increased viscosity [27].

The surfactant concentration, at which the sudden reduction of viscosity occurred, increases when the NaOct/CTAB molar ratio is decreased. The viscosity is minimized, due to charge neutralization, at a higher surfactant concentration than with pure ionic NaOct. From comparison studies, at fixed starch concentrations but variable surfactants concentration, it has been found that, at certain concentrations of surfactant from potato starch, mixed ionic surfactant surface tension value is minimum. This indicates that maximum cleansing activity appeared at the mentioned points.

Figure 4 shows the variation of molar ratio of two surfactants' log conc. vs reduced viscosity curves. Increasing the molar ratio, the reduced viscosity decreased. This indicates an increase of strong interactions.

At concentrations considerably above those corresponding 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 dotted line in Figs. 3 and 4. Phase separation takes place at higher surfactant concentrations when the fraction of NaOct increases (Fig. 3). Increasing the mole fraction of NaOct above 0.83 does not significantly affect the CMC, but the two phase area extends to higher concentrations.

Figure 4 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 is reached in the order NaOct<CTAB<SDS<Triton X-100.

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, the higher is the redissolution rate.

Potato starch with ionic surfactants called "semi-natural surfactant" is obtained and grown from soil which is totally chemical-free. Detergent is a fully-chemical substance, synthesized from industry. Thus, detergent is seriously harmful for water-living organisms: like insects and fish. Semi-natural surfactants from potato starch are biodegradable, so they are eco-friendly. Our synthesized semi-natural surfactant is partially safe for fish and other animals, because it is biodegradable, partially chemical-free, and, finally, safe to the fourth generation: that is green chemistry.

H-bond formation with surfactant

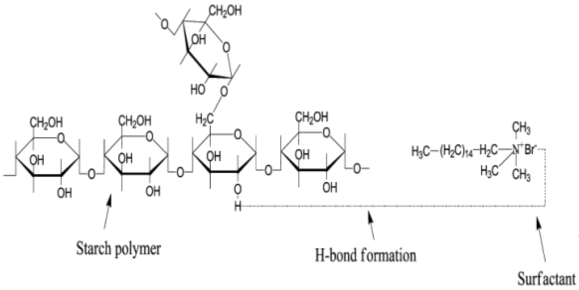


Fig. 5.H-Bond formation starch with cationic surfactants.

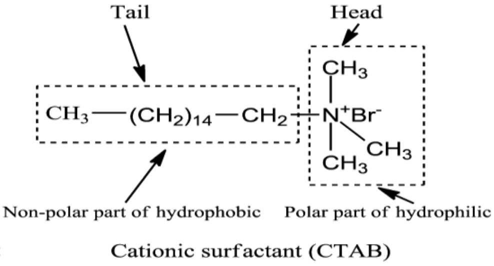
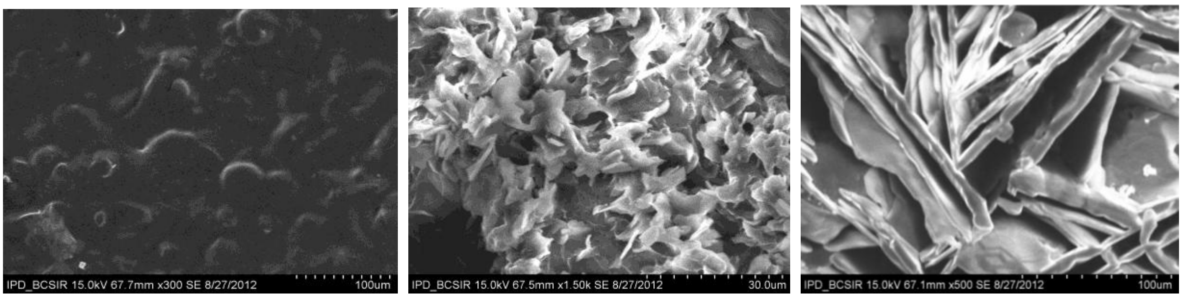


Fig. 6. Only-cationic surfactant molecule.

From Figs. 5 and 6, it can be seen that potato starch molecules have many hydroxyl groups and hydrogen atoms. These bind with surfactant molecules through H-atoms, which is called “intra- molecular H-bond formation” [28]. So bond breakdown is easy for both hydrophilic and hydrophobic parts of the surfactant molecule. Finally, cleansing activity increases although starches are biodegradable and eco-friendly.

3.1 Scanning Electron Microscopy (SEM)

Figures 7(a-c) show the individual surface images of starch, SDS and starch-SDS mixture, respectively studied by SEM. It can be seen from Figs. 7(a-c) that the surface images of the starch and surfactant are quite different. The surfaces of the starch, SDS and the mixture of these two look like granules, pop-corn and needles, respectively. A similar effect was observed in the case of other surfactants. It is clear that, at a certain temperature and concentration, the starch interacts with the surfactant through the formation of H-bonds and changes its surface structure [27].



(a) Starch **(b)** Surfactant (SDS) **(C)** Starch with SDS mixture

Fig.7. SEM Image of (a) Starch, (b) surfactant (SDS) and (c) starch with SDS mixture [28].

3.3 FT-IR Spectroscopy

It is always difficult to visualize the fundamental mode of vibrations of polymeric molecules like potato starch or chemical surfactants. Hydroxyl groups from potato starch showed 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, were found in our research.

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, such as temperature, environmental moisture etc. In *spectra* of starch and surfactant complexes, both have hydroxyl groups with sharp peaks at 3400 cm^{-1}.

Yet in the case of only non-ionic surfactant in Fig. 8c, there was no extra peak for the hydroxyl group. Both CTAB and SDS are ionic surfactants and interact with starch. A sharp absorption peak is present, which indicates that starch molecules form complexes with them.

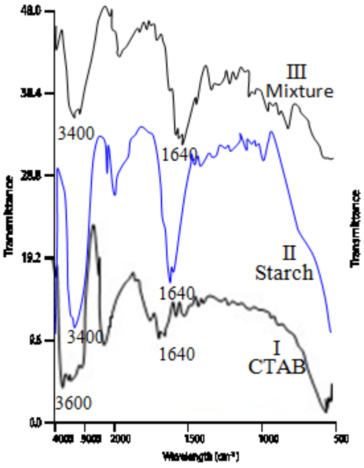


Fig. 8 (a) FTIR Spectra of I: Cationic (CTAB) Surfactant, II: Starch and III: Their mixture [27].

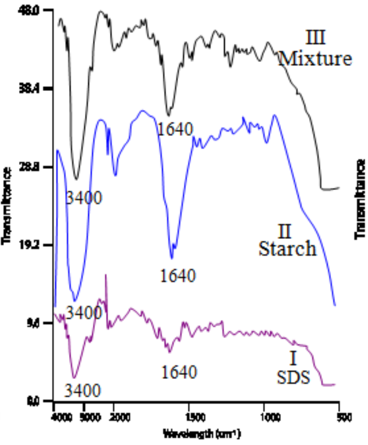


Fig. 8 (b) FTIR Spectra of I: Anionic (SDS) Surfactant, II: Starch and III: Their mixture [27]

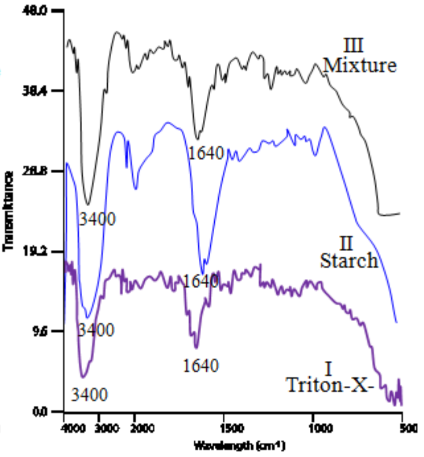


Fig. 8 (c) FTIR Spectra of I: Non-Ionic (Triton-X-100) Surfactant, II: Starch and III: Their mixture

From the IR spectrum of Fig.8. (a, b and c), the following peaks we could recognize

The influence of ionic surfactant concentrations on properties of starch based films was analyzed by FTIR spectra. Starch films with and without surfactant appeared smooth,

The influence of ionic surfactant concentrations on properties of starch-based films was analyzed by FTIR *spectra*. Starch films, with a thickness of 120-160 µm, with and without surfactant, appeared smooth, clear and transparent. The FTIR *spectra* of a starch film, individual surfactant and their mixtures are shown in Fig. 8(a-c). The broad absorption peak at 3260 cm^{-1} is due to the stretching frequency of the –N-H group [29] which overlaps the-OH stretching region at 3480-3440 cm^{-1}. *Spectra* of CMC films showed peaks at 1592 cm^{-1}, attributable to anti-symmetric vibration of COO^{-} groups [30,31].

Addition of ionic surfactant (CTAB, SDS) concentrations to potato starch films resulted in similar characteristics in the FTIR *spectra* (Figs. 8(a,b). This indicated that the anti-symmetric and symmetric vibrations of C=O and C-O bonds were enhanced, This enhancement was probably due to the disruption of intermolecular H-bonds between polar groups present in CTAB and SDS molecules, caused by added potato starch [29].

The symmetric COO- stretching was found at ~1411 cm-1 in all film samples. 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 with SDS addition. The ester bonds were mostly formed between the hydroxyl groups in amylopectin branches of starch and the 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 FT-IR spectra of rice flour-CMC blended film [32], chitosan-cassava starch-gelatin films [33], and corn starch-CMC-nano clay bio-composite films [34]. Non-ionic surfactants, mixed with non-ionic polymers, show a segregative phase separation [35].

The introduction of charged groups strongly influences the phase separation phenomena. Even a slight charge, on either polymer or surfactant, strongly enhances polymer-surfactant miscibility. Ionic surfactants tend to associate with non-ionic polymers. A mixture of two oppositely charged polyelectrolytes shows strongly associative behavior and there is a strong tendency for phase separation to occur [35,36].

However, it is clear that simply halting the production of solvents would do more harm than green chemistry would do benefit. Therefore, it is necessary to find some alternatives to the traditional methods used, whether greener solvents (semi-natural polymer solutions) are introduced, solvents are removed from the process altogether or alternative solvent systems are adopted for the next generation.

IV. Conclusion

The experiments reported in this paper show that strong ionic interaction occurs between cationic or anionic surfactants (CTAB, SDS), except nonionic surfactants (Triton-X-100) and starch polymers. This interaction leads to phase separation and precipitation of the formed amorphous complexes. Complex formation of starches depend on their 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 substance, containing 40 to 60% water. The high and low water contents of the complexes phase indicate that the interactions between the potato starch and ionic surfactants (SDS, CTAB) are very strong and they are capable of intermolecular H bonding.

Such bonding easily breaks down other bonds, which is more-effective cleansing than normal detergent. Yet, unlike detergents, these complexes are green chemistry: they are biodegradable and eco-friendly.

Green chemistry is concerned with improving the environment and fostering sustainable development. Our objectives have been achieved in this study; semi natural detergent is more powerful and safe for green chemistry. It finally challenges the quality of traditional methods of washing, cleansing and proper coloring of clothes. It seeks to provide solutions to the problems traditional chemistry faces.

The ionic surfactants (CTAB, SDS), at concentrations above their critical micelle concentrations (CMC), reduce the inter-polymer association, through micelle formation around hydrophobic (alkyl group length) groups. The presence of a miscible starch molecule also reduces inter-polymer association by preferential solvation of the hydrophobic groups.

One of the most challenging problems facing the world today is that of polymers, like potato starch: to use and build them up in the field of safe cleansing. It is up to firms to wholeheartedly begin the transition away from polluting petrochemical polymers like surfactants and embrace a new generation of sustainable, biodegradable, competitive and economical semi- natural surfactants from potato starch. Such new surfactants are needed by future generations to rescue us from global warming. Just like “totally CFC and chemical free” in the 1990s, let “semi-natural” be the words that consumers look for in choosing a detergent in the 21st century.

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