



Cleansing Activity of Polymeric Starch by Reducing the Environmental Hazards to Safe Green Chemistry

By Md. Mohsin Hossain & Md. Ibrahim H. Mondal

University of Rajshahi, Bangladesh

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Keywords: starch, surfactants, cmc, biodegradable, cleansing, XRD and SEM, green chemistry.

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Md. Mohsin Hossain ^α & Md. Ibrahim H. Mondal ^σ

Abstract- The bio-degradable starch interaction with various surfactants has been studied for the investigation of ability and cleansing activity of starch-surfactant-water system. The surfactants investigated were sodium dodecyl sulphate, sodium octanoate, cetyltrimethyl ammonium bromide 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 which also indicated the more cleansing activity of polymeric starch (potato) were cheaply available indoor market in Bangladesh. Biodegradable starch interactions with ionic surfactants by the way of H-bond formation to ensure complexation and reduced the harmful criteria of living organism also to ensure maximum protection of our green chemistry. The formed complexes were analyzed and characterized by FTIR spectroscopy, XRD and SEM instrument. Some of the complexes exhibited excellent emulsifying efficiency and surfactants performance properties with this biodegradable starch polymer.

Keywords: starch, surfactants, cmc, biodegradable, cleansing, XRD and SEM, green chemistry.

I. INTRODUCTION

The cleansing activity of soap-detergent is one of the most important phenomena in daily life for the modern society. Thus the improvement of activity of soap-detergent is obviously required for the better quality and performance. Green biodegradable polymers derived from natural resources are potentially very interesting substitutes for non - biodegradable petroleum - based polymers. An attractive field of

application for these polymers is the 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 particular starch is attractive as it is relatively cheap and abundantly available. However, the use of native starch for packaging materials is limited due to its low moisture resistance, poor processability (high viscosity), high brittleness, and incompatibility with hydrophobic polymers. Further modification of starch is therefore required to introduce hydrophobicity and to improve mechanical and moisture barrier properties. Thus the interactions may be intra and/or intermolecular. The balance depends on the structural parameters of the polymer, such as the nature, lengths 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], hydroxyethylcellulose, carboxymethyl cellulose [5], [6] and pullulan [7]. Increasing interest has been focused on the structure– solution property relationship of amphiphilic polysaccharides [8], [9], [10] and [11]. The associative behaviour of hydrophobically modified carboxymethyl cellulose and Carboxymethyl pullulan (CM-pullulan) were studied after the amidation of these polysaccharides in DMSO [10], [7]. In previously studied, the hydrophobization of various polysaccharides were investigated, such as hydroxyethylcellulose [12] carboxymethyl cellulose [13], xylan [14], and carboxymethyl starch [15], [16] by the esterification of hydroxyl groups using classical (with acylchloride and mixed anhydride) and unconventional methods.

The interactions of surfactants with cationised cellulose, has been studied by [17], [18] and nonionic cellulose ethers have been subject of extensive studies by [19]. The structure of starch is very similar to cellulose, but the difference on the bindings, which link

Author ^α ^σ: Polymer and Textile Research Lab., Department of Applied Chemistry & Chemical Engineering, University of Rajshahi, Rajshahi, Bangladesh. e-mail: mihmondal@yahoo.com

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 Rowen and co-worker [20] and [21] 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 is proved 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 with various surfactants and the better understanding the mechanism between starch and surfactants complexes studied by the ternary phase diagram, interfacial surface tension and viscosity measurement and characterized by the XRD and SEM analysis.

II. EXPERIMENTAL

a) Materials

Potato starch as powder form was purchased from UNI-CHEM, China and 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 min.

All solutions were prepared at least 24 h before measurement was performed. The surfactants sodium dodecyl sulphate (SDS), N-cetyl- N,N,N-trimethyl ammonium bromide (CTAB), sodium octanoate (NaOct) and Tween 20 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 $71.5 \times 10^{-3} \pm 0.5 \text{ N/m}$ at 30°C. All other chemicals were analytical grade and were used without further purification.

b) Methods

i. Surface and Interfacial Tension Measurement

Surface tension was measured with a drop weight method (Stalagmometer instruments). In the

calculation of surface tension, the correction factors of Huh and Mason [22] were used. The reproducible result between measurements of the same sample was $\pm 0.5 \text{ mN/m}$. The results of the surface tension measurement were presented as (γ) values calculated from $\gamma = \frac{mg}{2\pi f}$.

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.

c) Viscosity

Viscosities were determined with an Ostwald viscometer according to British standard (Fisher Scientific TM 200) with a fluctuation of $\pm 0.10 \text{ C}$ 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

calculated from $\eta_{red} = \frac{(t-t_0)}{t_0} \cdot \frac{C}{c}$, 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 & surfactants mixed polymer.

d) Ternary Phase Diagram

For the development of ternary phase diagrams, the sample components were taken into the test tube by varying composition in such a way that the total composition remains 100%. The components were added by varying weight or volumes. The samples were prepared by varying 5% composition of two components simultaneously keeping the third component constant, alternatively in a test tube. The open end of the test tube was then closed with rubber cork in such a way that the vapour would come out and would enter into the test tube, here the cork reacted with the sample. The samples were then shaken for well mixing of the components and placed into the diagram are put 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, so that this would

remain no leakage or the lower part of the cork did not touch the sample solution and after that these samples were then left to equilibrate in a thermostat box at 30°C for at least ten days and would be shaken from time to time. The equilibrium was established within this period.

e) Characterization

i. SEM Analysis

Scanning Electron Microscope (SEM, JEOL, JSM 6301F, Japan), Fine coater (JFC 1200, JEOL, Japan), Aluminum specimen stub, Double-sided adhesive tape.

ii. Procedure for Sample Determination

Scanning Electron Microscope (SEM) of potato starch, surfactant sample and starch-surfactant complexes samples were less than 4% moisture content before examined. Dried sample and sprinkle were 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 seconds. The coated sample was then placed in the sample chamber of the SEM (Appendix Fig.7.1). The sample was examined at magnification of 2,500 and 6,000 with the accelerating voltage of 10 Kv.

Model and Specification

iii. XRD Analysis

iv. Preparation of Sample for XRD

The preparation of starch sample, the dried sample is saturated with water by stirring repeatedly with a glass rod; this step is performed by 2g of starch with 100 ml of hot water which is 100% distilled and stirred at room temperature for 1h, centrifuging the suspensions and decanting the supernatant solutions. This process is repeatedly three times. Then the starch solution is dried in oven at temperature 80°C. 2h after proper drying the powder sample is kept in a sealed bottle. The syntheses of cationic surfactants were undertaken by the following procedure: 2g of Sodium dodecyl sulfhate was first dispersed in 100 ml of de ionized water then under mechanical stirring for about 1h. A pre dissolved starch solution of same amount was slowly added to that suspension near about at 80°C. The reaction mixtures were stirred for 1h at 80°C using mechanical stirring after proper drying the powder sample is kept in a sealed bottle then dried products were stored in vacuum desiccators.

Starch powders to be used for X-ray diffraction (XRD) measurements were equilibrated in desiccators containing saturated solutions of K_2CO_3 at 20-22°C. Under these conditions, the relative humidity (RH) at 20°C was shown to be 44% and the final water content of pea, maize, potato, and wheat starches was 13-14, 12, 15, and 12%, respectively. Wet starch powder (from potato) for XRD measurements was produced by first equilibrating the starch in excess water. The starch

suspension was then centrifuged (3000 *g*) and the supernatant removed. The starch precipitate appeared as a hard wet powder that was slightly more moist at the top. This moisture was dried with tissue paper. The wet starch powder had a water content of 49%. It was apparent that the proportion of water was slightly overestimated, because the precipitated starch granules would have a small amount of free space between them, which would be filled with free water. This overestimation, however, can be considered to be very small as the granules in the precipitate were closely packed. Since the water content within the crystallites is fixed, near about 24% the proportion of water in the amorphous part of starch can be estimated at 55- 60%. It was assumed that total crystalline of starch and complexes.

Apparatus Wide-angle X-ray diffractometer (JEOL, JDX 3530, Japan), Silicon sample cell and Computer with program MDI Jade 6.5 (Japan).

III. RESULTS AND DISCUSSIONS

Some of the prepared starch-surfactant mixture lowered the surface tension of water, namely at lower concentration of the sample (Table 1). The functional properties of some of the prepared surfactant and starch mixed surfactant solutions were tested for emulsifying efficiency, washing power and antiredeposition efficiency. The emulsifying efficiency was characterized by the stability of the parafinic Tween-20/water emulsions and other surfactant mixture at definite ratio. The results summarized in Table 2 which show that some of the surfactant made emulsions of the oil/ water type stable even after 24 h. Their 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 antiredepositive efficiency was higher than the starting SDS, but moderate in comparison to starch used as a co-builder in detergents [23].

Table 1 : The Value of Surface Tension of Surfactants (Cationic, Anionic and Non-Ionic)) with Added Starch

% Log Conc. of surfactant solution	% Conc. of surfactant solution	Surface tension of SDS mixed with starch soln.	Surface tension of CTAB mixed with starch soln.	Surface tension of Tween-20 mixed with starch soln.
-2.00	0.01	49.11	49.19	53.11
-1.69	0.02	48.02	47.15	50.19
-1.52	0.03	45.35	45.67	49.75
-1.39	0.04	44.31	44.89	48.61
-1.30	0.05	43.13	44.15	46.63
-1.22	0.06	42.95	43.37	45.84
-1.15	0.07	42.73	42.69	45.45
-1.09	0.08	42.55	42.46	45.05
-1.04	0.09	42.52	42.45	44.05
-1.00	0.10	41.51	42.41	44.07

Table 2 : At Temperature Ranges (25o-85oc) Solution Viscosity of Starch Mixed Surfactant CTAB

Temp °C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.50%	1.0%
25	1646.523	810.610	417.380	211.138	118.29	1545.39	910.251	534.50	288.45	181.67
35	1380.073	821.446	471.486	289.594	180.15	1291.59	756.736	414.09	248.74	148.57
45	1214.395	778.756	421.537	248.772	161.83	1171.50	700.102	332.94	226.80	133.51
55	1073.070	640.599	364.620	238.510	130.61	1011.82	603.996	366.08	182.87	124.72
65	920.668	571.382	381.039	208.818	128.11	911.044	546.011	367.44	158.34	103.61
75	847.704	529.308	319.558	184.321	114.53	812.917	468.325	249.96	155.25	98.76
85	746.026	478.272	286.076	168.94	99.96	753.728	441.672	252.48	141.58	89.44

Table 3 : At Temperature Ranges (25o-85oc) Solution Viscosity of Starch Mixed Surfactant SDS

Temp °C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.50%	1.0%
25	1646.523	810.610	417.380	211.138	118.29	1545.39	910.251	534.50	288.45	181.67
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45	1214.395	778.756	421.537	248.772	161.83	1171.50	700.102	332.94	226.80	133.51
55	1073.070	640.599	364.620	238.510	130.61	1011.82	603.996	366.08	182.87	124.72
65	920.668	571.382	381.039	208.818	128.11	911.044	546.011	367.44	158.34	103.61
75	847.704	529.308	319.558	184.321	114.53	812.917	468.325	249.96	155.25	98.76
85	746.026	478.272	286.076	168.94	99.96	753.728	441.672	252.48	141.58	89.44

Table 4 : At Temperature Ranges (25°-85°C) Solution Viscosity of Starch Mixed Surfactant Tween-20

Temp °C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625	0.125%	0.250%	0.500%	1.000%
25	102.783	96.837	101.702	114.032	102.783	134.877	106.567	149.427	116.297	171.765
35	86.567	81.162	102.921	98.346	120.374	113.503	144.299	120.367	170.153	157.970
45	76.837	73.594	89.849	87.888	106.633	98.236	123.786	108.401	151.884	135.538
55	66.567	63.864	80.699	76.124	93.656	86.022	109.256	96.435	133.615	123.843
65	57.918	57.378	71.549	67.627	85.259	76.862	100.709	84.470	121.115	107.654
75	53.594	51.432	65.666	61.091	78.389	69.992	92.162	77.632	110.538	98.976
85	48.189	47.108	59.784	55.209	71.519	63.122	84.470	70.794	99.961	87.378

Several references may be found in the literature to the compaction of poly electrolytes on binding of oppositely charged surfactants [24]. Viscosity measurements have been carried out by [25] on mixtures of PSS of Mw of 130 000 and DTAB. When added to solution of 0.36 w% PSS, DTAB in the pre-precipitation zone brought about a progressive reduction in the viscosity of the solutions. For example, 5.8 mM DTAB was found to drop the reduced viscosity of PSS by a factor of ten, far exceeding the reduction effected by addition of the simple analog "surfactant", tetradecyltrimethyl ammonium bromide. The explanation offered was that coiling of the flexible "vinyl" backboned

poly electrolyte occurs around small clusters of the surfactant, which form under these conditions. Similar effects have been obtained by [26] who studied the viscosity characteristics of a series of amphoteric polymers on addition of anionic (SDS) or cationic (CTAB) surfactants to their solutions. [27] and [28] have reported viscosimetric and rheological studies on two cationic polymers, viz. a cationic cellulosic (Polymer JR) and an acrylamide/methacryl oxyethyl trimethylammonium chloride co-polymer (Reten, Hercules) within a range of polymer and added SDS concentrations. Considerable differences in behavior between the two polymers were found.

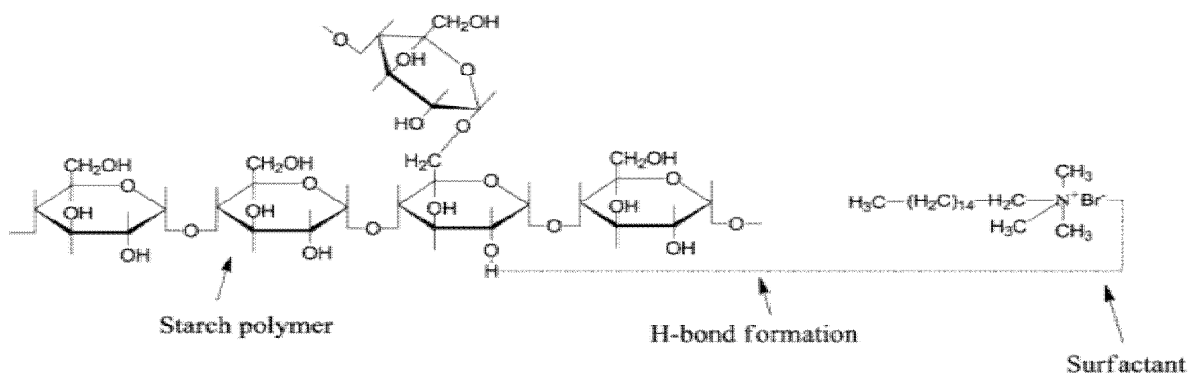


Fig. 1 : H-Bond Formation Starch with Cationic Surfactants

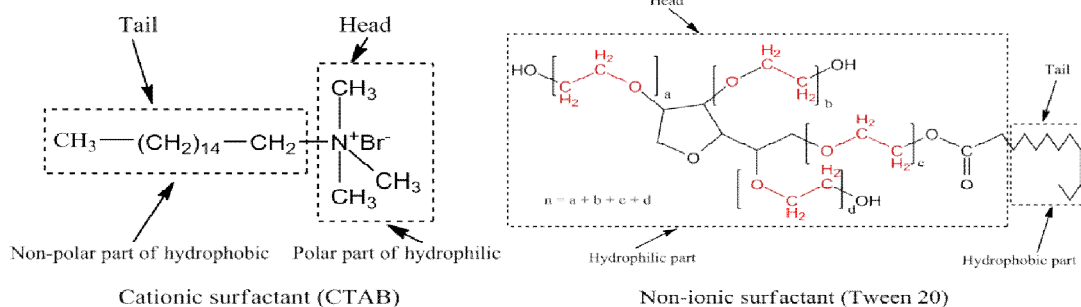


Fig. 1 (a) : Cationic Surfactant Molecule Fig. 1(b) : Structure of Non-Ionic Surfactant Absence of Polar Part

From Fig.1 it has been found starch molecule have many hydroxyl group and hydrogen atom which bind with surfactant molecule through H-atom called H-bond formation. So bond breakdown is easily of hydrophilic and hydrophobic part of surfactant molecule finally cleansing activity increased although starch are biodegradable and eco- friendly. Our motivation for the present study is not only scientific interest. Poly soaps are present in the wash liquor where they might form micro domains. Amphiphilic molecules may bind to these domains, and the concomitant reduction of free surfactant in solution may adversely affect wash performance of surfactants. The Fig.2 (b) of non-ionic surfactant under the region given where it has been

seen that the non ionic Tween -20 molecule is totally dipole absent so, there is no chance to make bond formation through H atom by hydrogen bonding with starch molecule.

From results analysis it has found at lower concentration the reduced viscosity value are high but at CMC point the curve become level off but after increasing concentration the reduced viscosity value increased slowly in all cases but in case of ionic surfactant (SDS, CTAB) the changing is remarkable due to maximum interactions occurred with starch polymer. Here, we mentioned that temperature has a remarkable effect in the complexes of starch-ionic surfactant, here it is obtained according to Arrhenius rule increasing

temperature reduced viscosity and specific viscosity is reduced due to the freeness of solution.

From Viscometric analysis The viscosity of the larger scale formation of complexation were measured at 100 rpm was lower than the experimental-scale (13.5 ml starch solution) but not significant difference ($P > 0.05$) with an approximately $1,785.15 \pm 13.18$ and $1,790.50 \pm 12.21$ cP, respectively. The lower the viscosity, the less was tendency for any further spontaneous reduction with surfactant mixture.

From the Tables 2 to 4 we are trying to identify the differences among the ionic and non-ionic surfactants in presence of polymeric starch the results show different between the respective two types surfactants. Not only this Triton-X-100 and Tween-20 are the non ionic but SDS and CTAB are ionic. Comparable study Ionic surfactants showed excellent results as reduced viscosities value and specific viscosities values. Here, we have been found that the increasing temperature the values of reduced viscosity and specific viscosity has decreased due to freeness of bonding in the complexes as a inclusion compound in between starch and ionic surfactants but in case of Triton-X-100 and Tween-20 no bond formation is formed due to the absence of dipole in that respective two non ionic surfactants (Fig.2(b)).

From the Fig.3 (a) it has been seen five distinct phases and they are 1L, S+L, LC, LC+S and S The one liquid phase is shown in the area ayb. This phase indicates 15% starch is solubilized in water / starch boundary line. The boundary line of CTAB / water indicates 25% of CTAB solubilized in this phase, the Solid + liquid phases are described by the area abcd. In the S+L phase water/CTAB boundary line, CTAB is 55 to 75% solubilized and starch is 25 to 65% solubilized in this phase. The most important and interesting liquid crystal phase (LC) is denoted by the region dcef. in the LC phase. 45 to 55% of CTAB is solubilized on the water/CTAB boundary line and also starch is 35 to 65% solubilized on the water/starch boundary line, LC+S phase: In this phase is shown in the area efgh. It is the big region and CTAB is 25 to 45% solubilized in the water/CTAB boundary line and starch is 65 to 95% solubilized on the water/starch boundary line and In the

corners of starch and CTAB the Solid phase is formed. The region of this phase is ghxz. S, The solid phase waists toward CTAB and starch corner but this area is most inactive where no interactions occur.

From the Fig.3 (b) it has been seen five distinct phases and they are 1L, S+L, LC, LC+S and S The one liquid phase (1L) has shown in the area ayb. This phase indicates 17% of starch is solubilized in starch/water boundary line. The boundary line of water / SDS shows that 25% of SDS has solubilized in the 1L phase. The solid + liquid phase (S+L) is denoted by abcd. The S+L phase formed is relatively small. The most important and interesting liquid crystal phase (LC) is denoted by the region cdef. In the LC phase 35 to 36% of starch is solubilized in the water /starch boundary line and less than 9 to 10% SDS is solubilized in this phase. The remaining big region denoted by efgh is the liquid crystal and solid phase. In this phase, water / SDS boundary line shows to 54 to 55% SDS and starch / water boundary line shows 65 to 95% starch is solubilized in this phase. The remaining region gxzh is the solid phase, S which is unreacted area. From the Fig.3(c) it has been seen three distinct phases and there are:- 1L, S+L and S. In the 1L phase 7.5% starch is solubilized. Above the 1L phase a large region ydac of S+L phase is formed. In the S+L phase the maximum of starch is 75%. In the region azc is the small area where only solid phase, S is found. The phase area is minimum. Though Tween-20 is liquid sustenance, its interaction is different from other ionic (CTAB, SDS) surfactant with natural polymeric starch. In this ternary phase there is no crystalline phase due the non ionic surfactant of Tween-20. In this phase there is no change in the region ydx, here any type of chemical reaction did not occur due to non-ionic surfactant of Tween-20. From Fig.(c) it have been seen that as a non ionic surfactant of Tween-20 any chemical reactions, H-bond formations, any type of crystallinity has not seen in Fig.3(c) not form which support Tween -20 have no effect on starch like polymer for better interactions. Adding starch on surfactant, the reaction mechanism can be explained here due to the complex formation in between amylose and ionic surfactant through the H- bond formation. Here, it is mentioned that from SEM

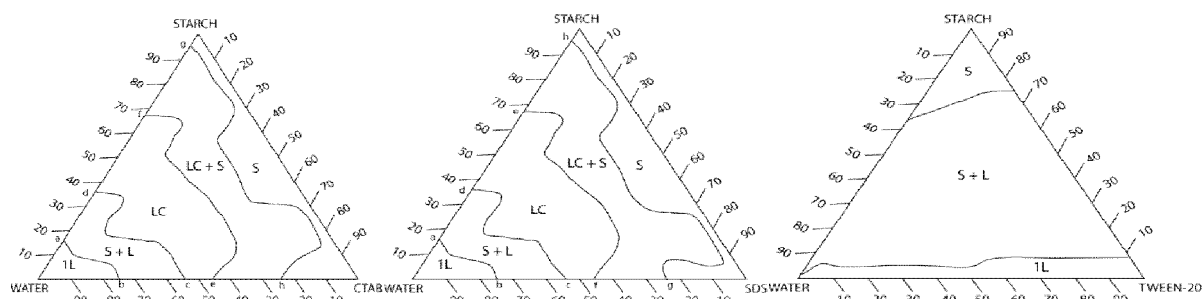


Fig. 3(a) : Starch+ Cationic CTAB+H₂O (b) Starch+ Anionic SDS+H₂O (b) Starch+Non-Ionic Tween-20+H₂O

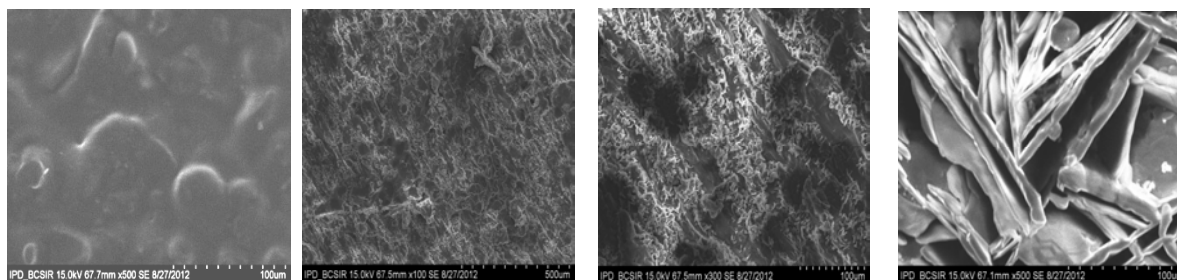


Fig. 4(a) : SEM Image of Starch (b) SEM Image of SDS (c) SEM Image of CTAB (d) SEM Image of CTAB+ Starch

various type of rupture are found on the surface area of complexes compared to other homogeneous surfaces obtained from SEM images of both individual samples.

From SEM Fig.4 (a), Fig.4(b) and Fig.4(c) have been found varieties types smooth, homogeneous surfaces but it is cleared to identify that in reacted starch-ionic surfactant complexes found in the Fig.4(d) has a lot of rupture region in the magnification area. Here, it has been identified smooth surfaces in only starch or only surfactant SEM image where as reacted complex film images showed a remarkable identity that have definite interaction may occur. So it is clearly decided that obviously interactions may occurred in starch and ionic surfactants complexes.

Amorphous and crystalline sections were examined from the X-ray diffractograms and the X-ray spectra are shown in Fig.5a. Peak baseline (white area) and smooth curve (bold area) were computer-plotted on the diffractogram which is shown in Fig.5b. The area above the smooth curve was the crystalline portion and the bold area above the peak baseline was the amorphous portion. The % crystallinity of complexes samples were calculated as the ratio of area of the crystalline sharp peak over the total area at angles between 10 and 90° using a computer program based on the methods of [29] Over all results discussions our observations are Starch/ surfactant interactions can be understood by assuming that the most important factors governing the behaviour on the systems are cooperative hydrophobic interactions between surfactant chains and

electrostatic interactions between cationic and anionic poly electrolytes Hydrophobic polymer /surfactant interactions are of minor importance. The enhanced surface activity of these systems at very low surfactant concentrations is due to formation of surface-active complexes by way of counter ion condensation.

Critical association concentrations are observed at concentrations well below the CMCs of the surfactants. There is a minimum hydrocarbon chain length of the surfactant and also a minimum degree of substitution of the starch to association between the starch and surfactant to take place. Associative phase separation occurs in extremely dilute systems when the charge ratio between the surfactants and the polymers is close to one. The effect of mixing on the micellization of the binary surfactant solutions can be described to a good approximation by taking into account only the effects of the volume difference between the hydrocarbon chains. Complex formation on starch with ionic surfactants depend on the chain-length difference in exactly the same way as for free mixed micelles. The separated complex phase is a hydrophobic, highly viscous and gel-like containing 40 to 60 w% of water. The high viscosity and low water content of the complex phase indicates that the interactions between the starch and ionic surfactants are very strong. The water content of the complex phase decreases when the chain length of the surfactant or the DS of the starch increases, indicating increased polymer/ surfactant interaction. With mixed surfactants the water content of

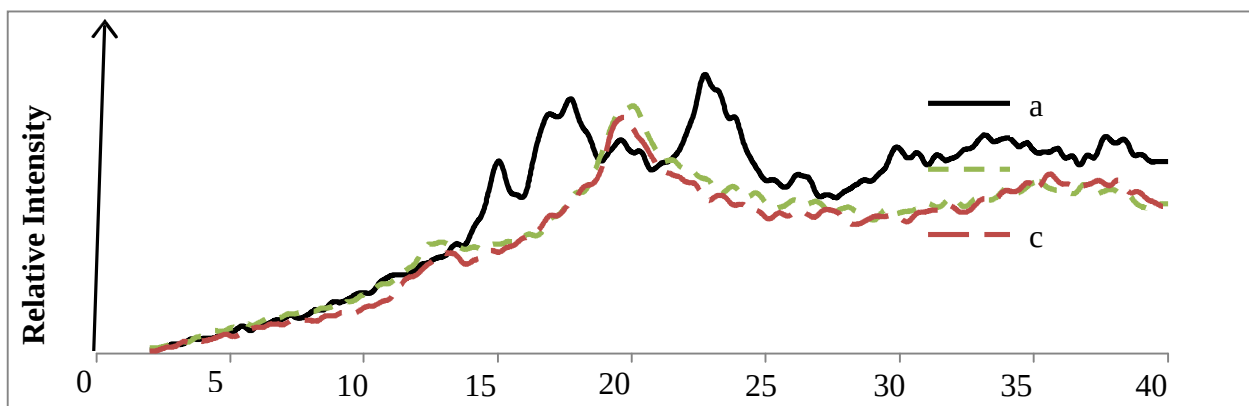


Fig. 5 : Calligraphy of X-ray diffraction patterns of **a**= black bold line normal potato starch, **b**= green dotted line Starch with CTAB and **c** = blue dotted line Starch with SDS

the complex phase increases when the chain length difference increases. The more surface-active component is strongly enriched in the polymer complexes. When excess surfactant is added, the separated complex phase redissolves completely or partly, depending on the charge density of the starch. XRD indicates that mixed micelles of alkanoates are prolate ellipsoids with the shorter chain surfactant enriched in the end-cups of the ellipsoid. XRD also indicates that in dilute solutions starch molecules are roughly cylindrical i.e. have helical conformation. When they associate with surfactants, aggregates are formed, in which a core of surfactant is surrounded by starch. The surfactant monomers do not form any micelle like aggregates in these complexes. The structure of the complexes resembles the inclusion complexes of amylose and surfactants. In mixed surfactant systems, the longer chain surfactant is enriched into the surfactant/starch complex. As the XRD results show, the charge equivalence starch/surfactant complexes consist of a lyotropic liquid crystalline phase. Depending on the chain length of the surfactant, temperature and concentration, the structure of the liquid crystalline phase is hexagonal, lamellar or cubic. The mesophases are the same as the pure surfactants in forming without any added polymer, but they form with starch at much lower surfactant concentrations. Thus, the polymer act as a huge and very effective counter ion that screens repulsion between the surfactant head groups and the surfactant aggregates. The gel-like starch/surfactant complex phases have high viscosity and elasticity. They show pseudoplastic behaviour. The rheological behaviour of the complexes is described by the Hershel-Bulkley model. The rheological data for the complex phases are compatible with the finding that the surfactants form liquid crystalline structures with the polymer anchored to the surfactant aggregates.

IV. CONCLUSIONS

Starch/surfactant interactions can be understood by assuming that the most important factors governing the behaviour on the systems are cooperative hydrophobic interactions between surfactant chains and electrostatic interactions between cationic and anionic polar part of Hydrophobic polymer /surfactant interactions are of minor importance. The rheological data for the complex phases are compatible with the finding that the surfactants form liquid crystalline structures with the polymer anchored to the surfactant aggregates by H- bond formation. In this study, the interactions between surfactants and starch have been investigated within different contexts. Systematic investigations such as: surface tension, viscosity and ternary phase on the effect of the surfactant structure (head group and chain length) on the temperature-induced changes of potato starch granules in excess of

water which reducing environmental hazards protecting our global green chemistry.

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