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Surface Properties of Water Soluble Surfactants, Starch and their Complexes by Various Methods

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Abstract. Surface, interfacial tensions and reduced viscosities were measured for water soluble surfactant and starch solutions in order to determine their potential as stabilisers, emulsifiers or cleansers. The surface tension and reduced viscosity for an acid hydrolysed starch (potato) initially were declined with concentration and then reached an equilibrium value of 56 mN/m and 3.1dm^3/mol, at 20-40 wt.%. Surface, interfacial tensions and reduced viscosity of starch with surfactant mixture using the ratio 40/60 decreased more rapidly with concentration reaching values of 41-44 mN/m, and 2.5dm^3/mol, respectively, at 40 wt.%. There was little dependence of surface or interfacial tensions on degree of substitution between 0.3-0.8 and amylose content of starch . Surface and interfacial tensions for starch /surfactants mixtures were lower than those for only starch, particularly at lower concentrations. Emulsions of soybean oil/water mixtures were successfully stabilised for >1 day by potato starch acetate/octenylsuccinate and acetate/ dodecenylsuccinate but not by starch and surfactants. Therefore, these starches may represent biodegradable, economically alternatives to some emulsifiers, soap or detergents filler with effective cleansing activity and coating polymers currently in use.

Keywords: starch, surfactant, surface tension, viscosity, emulsifier, cleansing

Introduction

The cleansing activity of soap detergent is one of the most important phenomena in daily life for the modern society. Thus the improvement activity of soap detergent is obviously required for 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 of packaging materials. For the current petrochemical based products recycling is often neither practical nor economically feasible (Thiebaud *et al.,* 1997). 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 processibility (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 or intermolecular. Hydrophobically modified water soluble polymers are useful in a number of areas, such as thickeners, coatings, emulsion stabilisers and detergents (Holmberg *et al.,*2002; Piirma,1992; Shalaby *et al.,*1991; Glass, 1989). The surface properties of these polymers are important to their function of intermolecular adhesion, spreading on surfaces and dispersing oils and other hydrophobic compounds. Presently research is focussed in replacing non degradable, petroleum based materials currently used with bio-based materials derived from renewable feed stocks (Swift, 2002). In particular, native and chemically modified starches have been prepared and studied for uses in these areas (Dokic-Baucal *et al.,* 2004; Tesch *et al.,* 2002; Srokova *et al.,* 2001; Ebringerova *et al.,* 2000; Viswanathan, 1999).

Surprisingly, there is relatively little published informa-tion on the surface and interfacial tensions of native and modified starches and existing data is conflicting or incomplete. Ray *et al.* (1958) and Scholz *et al.* (1958) determined critical surface tensions for wetting of 35-39 N/m for starch, amylose and amylopectin films, 40 N/m for amylose triacetate and approximately 32 N/m for starch tributyrate.

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Lawton (1995) reported contact angle data for various liquids on cast and extruded starch films and calculated surface energy values of 35-42 N/m using the harmonic mean method of Wu (1982); Wu and Brzozowski (1971). Using the same data and the van Oss/Chaudhury/Good (VCG) method, Biresaw and Carriere (2001) calculated a value of 43 N/m. Surface energies of 47-56 N/m were reported by Odidi *et al.* (1991) for discs made from compressed starch powder although surface roughness would be expected to influence the results. Krycer *et al.* (1983) measured a surface tension of 59 N/m for a 4% solution of corn starch in water. Rudolph and Glowaky (1978) found surface tensions of 36-60 N/m for dilute (1%) aqueous solutions of mixed (acetate/phthalate, propionate/phthalate, butyrate/phthalate) esters of hydrolysed starches of degree of substitution (DS) 1.56-2.3 (Rudolph and Glowaky, 1978). Interfacial tensions of 12-21 N/m were reported recently by Tesch *et al.* (2002) for 1-5% solutions of octenyl-succinate (USA) starch and vegetable oil but no information on the DS, molecular weight or preparation method for the USA starch was given. There have been no published reports on the surface properties of starch-surfactants of DS < 3 or mixed SDS/CTAB emulsifiers of starch.

The surface energy of starch is uncertain and there is little data or understanding of the effects of DS and concentration on the surface properties of starch derivatives. Part of the reason for this may be that most commercially available derivatives are low DS (<0.05) granular starches which tend to have poor solubility in water or other solvents. Recently, Shogren and Biswas (2006) reported a simple method for preparation of highly water soluble starch acetates and mixed esters using microwave heating under non aqueous, homogeneous conditions.

Though many researchers have paid their attention in this field but chemical reactions, bond formation on starch surfactants interaction are still open for discussion. The purpose of the present investigation was to explore the effect of starch interaction with various surfactants. Therefore, this study was taken to characterise the effects of SDS, Tween-20, NaOct and CTAB on the surface and interfacial tensions and reduced viscosities of aqueous starch solutions and to get better understanding of structure/property relations and help to determine feasibility of certain applications i.e., by the ternary phase diagram, interfacial surface tension and viscosity measurement.

Materials and Methods

Starch was synthesised by UNI-CHEM, chemical reagents made by China. The degree of substitution (DS) was 0.80. The starch was dissolved by heating the starch/water mixture in autoclave for 30 min at 120 °C. All solutions were prepared at least 24 h before measurements were performed.

Preparation of starch and mixtures. The basic procedure has been described previously (Swift, 2002). Typically, 70 g dry starch, 70 g CTAB, 7-35 g SDS, 0-7 g USA starch or 0-8.8 g Tween-20 were added to a 270 mL Teflon vessel. A magnetic stir bar was added and the mixture was stirred for 5 min. The vessel was then sealed, the thermocouple inserted and the vessel was heated in a ADVANTEC FC-610 forced convection oven (Milestone Inc., Shelton, Japan) from 25 to 150 °C over 3.5 min, then 150-160 °C over 1.5-2.5 min. After opening the reactor, the contents were placed in a Waring blender with 400 mL ethanol (99.5%) and blended until the precipitate was broken into fine particles. The ethanol supernatant was poured off and four additional ethanol extractions were performed. Excess ethanol was removed by filtration on a Buchner funnel and the starch surfactants mixture were dried in a forced air oven overnight at 50 °C and then in a vacuum oven overnight at 80 °C.

Surfactants. The surfactants used were commercial grade sodium dodecyl sulphate (SDS) and *n*-cetyl-*n*,*n*,*n*-trimethyl ammonium bromide (CTAB) were analytical grade made from LOBA Chemical Pvt., Ltd., India.

Other chemicals. The water was ion exchanged and distilled .Its conductivity, reduced viscosity was 2.0 μs, 4.0 dm^3/mol and its surface tension was 71.5±0.5 N/m at 30 °C. All other chemicals were analytical grade and were used without further purification.

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, 1975) were used. The temperature was 25 °C or 30 °C, depending on the Krafft point of the surfactants used. The reproducibility between measurements on the same sample was ± 0.5 N/m This was probably due to the very low concentrations of starch (0.01 wt.%). The results of the surface tension measurement were presented as (g) values calculated from

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

where:

$f = \frac{1}{v^3}$; v = volume of the drop; r = radius; m = the weight of falling drop; g = surface tension.

A drop of the weight (m) given by the above equation has been designated by Harkins and Brown (1919) as the ideal drop. Repeated measurements 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.

Viscosity. Ostwald viscometer of British Standard Institution with thermostat (the Fisher Scientific TM 200) with fluctuation of ± 0.1 °C was used to determine viscosities. 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 calculated from

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

where:

t = the measured efflux time of solutions; t_o = the efflux time of the pure solvent (water) and c = the weight concentration of the surfactant, starch and surfactants mixed polymer (starch).

Results and Discussion

The surface tension value of starch, surfactant and their mixtures are given in Table 1-3. Figures 1 and 2 show that starch molecule have many hydroxyl groups and hydrogen atoms which bind with surfactant molecule through H-atom called H-bond formation. So bond breakdown of hydrophilic and hydrophobic part of surfactant molecules finally increases cleansing activity. Although starches are surface inactive but due to H-bonding with ionic surfactants, it became more surface active which has proved the lowering value of surface tension and reduced viscosity at CMC point (Figs. 3-6). Tables. 1-3 also prove the gradual decreased condition of the value of surface tension but at CMC point the leveling value stops. Not only these, but CMC (critical micelle concentrations) have also been changed by the variation of mole fraction (Table 4).

From comparison studies at fixed starch concentration (0.01 to 0.1% w/v) and variable surfactants concentration (0.05, 0.15 & 0.45% w/v), it has been found that at certain concentration of surfactant surface tension, value is minimum which indicates maximum cleansing activity appearing in the mentioned points. It also shows from Figs. 5-6 log conc., *versus* surface tension plot at a fixed concentration (CMC) the value of surface tension is minimum but after increasing

Table 1. The value of surface tension (N/m) of all types of surfactants(0.05%) with added starch (0.01-0.1%) solution

% Log conc., of surfactant solution	% conc., of surfactant solution × 10^{-2}	Surface tension of SDS mixed starch sol^n. (N/m)	Surface tension of CTAB mixed starch sol^n. (N/m)	Surface tension of Tween-20 mixed starch sol^n. (N/m)	Surface tension of NaOct mixed starch sol^n. (N/m)
-2.00	0.01	50.61	50.44	50.36	50.13
-1.69	0.02	49.52	48.40	48.44	48.33
-1.52	0.03	46.85	46.92	47.00	46.59
-1.39	0.04	45.81	46.13	45.86	44.63
-1.30	0.05	44.63	45.40	44.87	44.15
-1.22	0.06	44.45	44.62	44.09	43.49
-1.15	0.07	44.23	43.94	43.70	43.23
-1.09	0.08	43.85	43.71	43.30	43.13
-1.04	0.09	43.82	43.70	43.75	43.11
-1.00	0.10	43.81	43.66	43.72	43.11

Table 2. The value of surface tension (N/m) of all types of surfactants(0.15%) with added starch (0.01-0.1%) solution

% Log conc., of surfactant solution	% conc., of surfactant solution × 10^{-2}	Surface tension of SDS mixed starch sol^{n}. (N/m)	Surface tension of CTAB mixed starch sol^{n}. (N/m)	Surface tension of Tween-20 mixed starch sol^{n}. (N/m)	Surface tension of NaOct mixed starch sol^{n}. (N/m)
-2.00	0.01	49.86	49.94	49.86	49.63
-1.69	0.02	48.77	47.90	47.94	47.83
-1.52	0.03	46.10	46.42	46.50	46.09
-1.39	0.04	45.06	45.63	45.36	44.13
-1.30	0.05	43.88	44.90	44.37	43.55
-1.22	0.06	43.70	44.12	43.59	42.99
-1.15	0.07	43.48	43.44	43.20	42.73
-1.09	0.08	43.10	43.22	42.80	42.63
-1.04	0.09	43.08	43.20	42.76	42.61
-1.00	0.10	43.08	43.20	42.76	42.61

Table 3. The value of surface tension (N/m) of all types of surfactants(0.45%) with added starch (0.01-0.1%) solution

% Log conc., of surfactant solution	% conc., of surfactant solution × 10^{-2}	Surface tension of SDS mixed starch sol^{n}. (N/m)	Surface tension of CTAB mixed starch sol^{n}. (N/m)	Surface tension of Tween-20 mixed starch sol^{n}. (N/m)	Surface tension of NaOct mixed starch sol^{n}. (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. 4. Critical micelle concentrations of binary surfactant mixtures (CTAB = cetyl sodium dodecyl sulphate and trimethylammonium bromide, NaOct = sodium octanoyate SDS

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	95.5	0.993	96.7	95.5	97.5	95.5

log conc., the results show that surface tension curve is level off. Present investigation is based on the critical micelle concentration (CMC) point and either any type of surfactants only or mixtures with starches, same results are found due to saturation and maximum interaction occurred in this points. Although, starch itself is surface inactive, however, when it has been added with surfactant as a soap or detergent filler, it

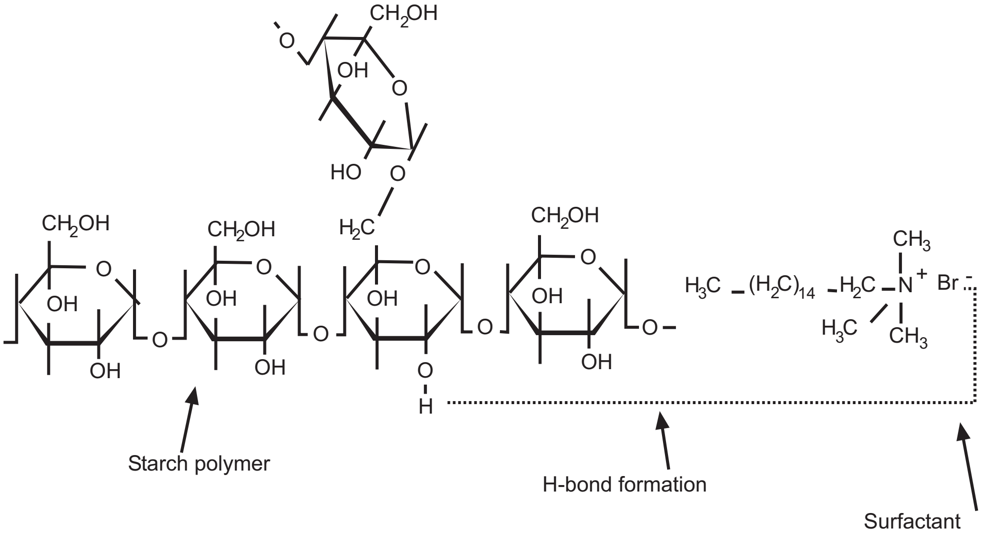
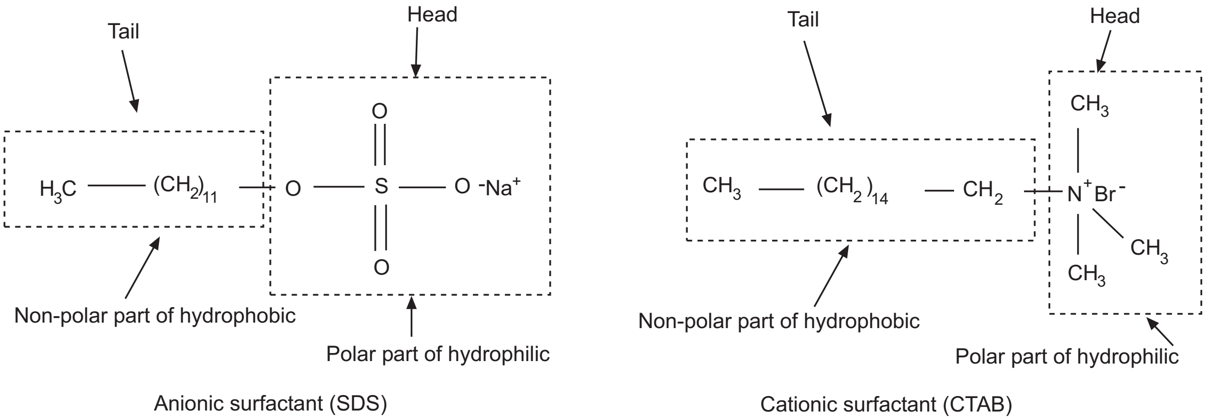


Fig. 1. H - Bond formation starch with cationic anionic surfactants.



Anionic surfactant (SDS)

Cationic surfactant (CTAB)

Fig. 2. Structure of both cationic and anionic surfactants having polar and non polar group.

reduces the surface tension value which means it reacts and makes bond formation like H-bond processes, where, both cationic and anionic of non polar part induced to break down the bond hence, it goes to dirty particle quickly which ensure prompt cleansing activity of starch mixed surfactant solution.

Figure 5 shows the surface tension of solutions of NaOct and NaOct/CTAB mixtures in 0.01 w/v starch solutions as a function of the surfactant concentration. Critical micele concentrations (CMC) are indicated by sudden changes in the slopes of the curves. When part of the NaOct is replaced by CTAB, the CMC increases with increasing mole fraction of the short-chain surfactant. 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 dashed line in Fig. 5 and 6. Phase separation takes place at higher surfactant concentrations when the fraction of NaOct increases (Fig. 6). 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. 5 shows the surface tension when a mixture of NaOct and shorter-chain surfactant is added (1:1mole 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 separates 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 in the shorter of the chain length of the second surfactant.

Figure 3 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 increases. Thus, the interaction depends markedly on the surface activities of the surfactants. The viscosity increase when excess surfactant begins to dissolve. At the same time, the added excess surfactant begins to form free micelles. This results in an increased viscosity. The surfactant concentration at which the sudden viscosity reduction occurs increases when the NaOct/CTAB molar ratio decreases. The minimum of viscosity due to charge neutralization also occurs at a higher surfactant concentration than with pure NaOct. The chemical

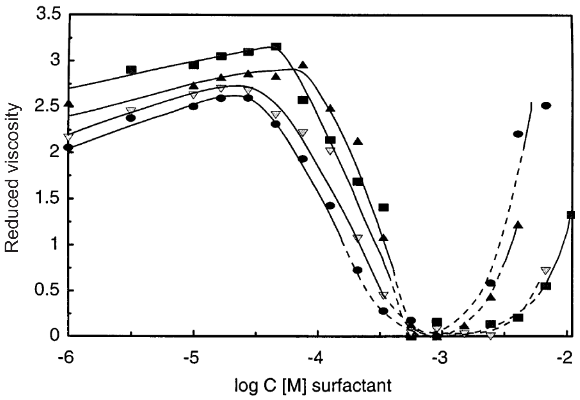


Fig. 3. Reduced viscosities of solutions of potato starch (0.01 wt.%, DS = 0.80) and Na Oct/ second surfactant mixtures. The surfactants were NaOct1 (●), NaOct/CTAB (▼), NaOct/SDS (▬), and NaOct/Tween-20) (▲). The molar ratio of the surfactants in the surfactants mixtures was 1:1. The two phase domain is indicated by the dotted line.

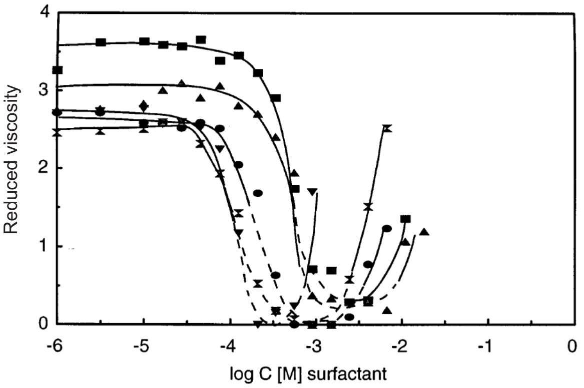


Fig. 4. Reduced viscosities of solutions of starch (0.01 wt.%, DS = 0.80) and SDS/CTAB mixtures. The molar ratio of the surfactants were 1:0. (▼), 3:1 (⧗), 1:1 (●), 1:3 (▲) and 1:5 (▬). The two phase domain is indicated by the dotted line.

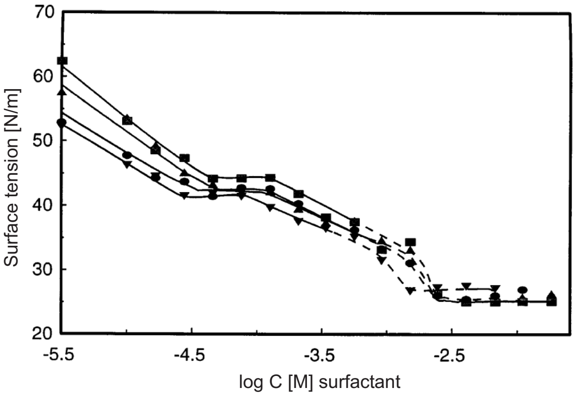


Fig. 5. Surface tension of solutions of potato starch (0.01 wt.%, DS = 0.80) and NaOct/second surfactant mixtures. The surfactants were NaOct (●), NaOct/CTAB (▼), NaOct/ SDS (▬) and NaOct/Tween-20 (▲). The molar ratio of the surfactants in the surfactant mixture was 1:1. The two phase domain is indicated by the dotted line.

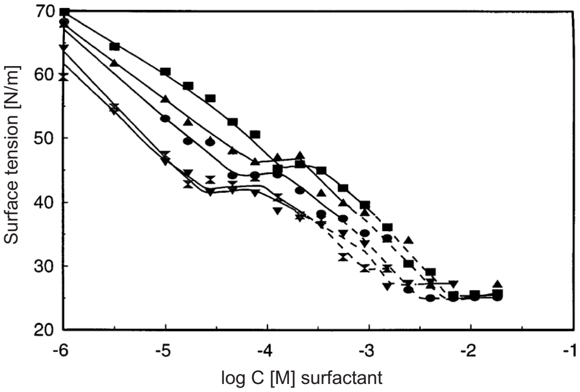


Fig. 6. Surface tension of solutions of potato starch (0.01 wt.%, DS = 0.80) and SDS/CTAB mixture. The molar ratio of the surfactants were 1:1 (●) 3:1 (⧗), 1:0 (▼), 1:3 (▲) and 1:5 (▬). The two-phase domain is indicated by the dotted line.

structures of the starch surfactants (SDS,CTAB) by the H-bonding process in Fig. 1-2. The efficiencies were high, typically 100% or higher, as reported previously (Shogren and Biswas, 2006). Values over 100% reflect direct esterification with acetic acid in addition to reaction with acetic anhydride. Reaction efficiencies of SDS (55%) and CATB (29%) were lower, reflecting the slower rates of reaction of starch with surfactants. Water solubility of the samples were >95% (w/w) except for high amylose starch which was 70%. For comparison, the water solubility of potato starch of degree of substitution was 0.03 prepared by the aqueous suspension method (Jeon *et al.,* 1999) was only 25%, even with prior heating and stirring an aqueous solution to 140 °C in a sealed reactivial. Reduced viscosities were low for potato starch and increased with amylose content as noted previously (Shogren and Biswas, 2006).

In models of mixed micellisation (Holland and Rubingh, 1992), the Gibbs energy of mixed micelle formation is discussed in terms of several contributions as follows:

(1) Contact energy of the surfactant. When the hydrophobic moiety of the surfactant is transferred from an aqueous environment into the liquid hydrocarbon like interior core of the micelle, there is a favourable change in the contact energy depending on the hydrocarbon chain length but is mainly due to the creation of water/water contacts.

(2) Conformational entropy. The transfer of the hydrophobic moiety of the surfactant into the micelles also implies an energetically favourable change in their conformational energy.

(3) Aggregate core-water interfacial Gibbs energy. If the hydrophilic moiety is not very bulky, the formation of a micelle generates an interface between the hydrophobic core region and the surrounding aqueous solution.

(4) Head group steric interactions: In the formation of micelles, the polar head groups of the surfactant molecules crowd into the aggregate surface. This generates steric repulsions between the head groups.

(5) Head group. Ionic and dipole interactions for ionic surfactants, repulsing electrostatic interactions arise at the micellar surface for zwitter ionic surfactants. One has to consider the interactions between the permanent dipoles of the polar groups.

Conclusion

The investigations presented in this paper show that strong ionic interaction between cationic and anionic surfactants (CTAB, SDS, Na Oct) 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 and is exactly in the same way as for free mixed micelles .The separated complex phase is a hydrophobic which is 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. The ionic surfactants (CTAB, SDS, NaOct) at concentrations above its CMC 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 solvation of the hydrophobic groups.

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