

Interactions between cationic starch and anionic surfactants
2. Viscosity and aggregate size in dilute solutions

Juha Merta, Per Stenius *

Laboratory of Forest Products Chemistry, Department of Forest Products Technology, Helsinki University of Technology,
Vuorimiehenhte 1 A, 02150 Espoo, Finland

Received 5 August 1996; accepted 5 August 1996

Abstract

The effects of the charge density of the polymer, the chain length of the surfactant and the ionic strength on the
viscosity and particle size of cationic starch/surfactant/water systems were investigated. Critical association con-
centrations (CAC) were observed at concentrations well below the CMCs of the surfactants. A strong decrease in the
viscosity at concentrations just below the phase separation concentrations is observed. Associative phase separation
occurs in extremely dilute systems when the charge ratio between the surfactants and the polymers is about one. The
separated phase is a highly viscous gel phase containing less than 60% water. Depending on the charge density, the
gel dissolves entirely or partly when excess surfactant is added. The properties of the systems can be understood
qualitatively assuming that (1) formation of surface active complexes through ion condensation occurs in very dilute
solutions, (2) the driving force of association of the surfactants with the polysaccharide chains increases as the
hydrophobic chain length of the surfactant or the charge density of the polyelectrolyte increases, and (3) there is an
associative interaction between the surfactant aggregates and the polysaccharide which decreases with increasing
ionic strength.

Keywords: Aggregate size; Cationic starch and anionic surfactant interaction; Viscosity

1. Introduction

Polysaccharide/surfactant interactions in aqueous solution have recently been studied rather extensively, and several reviews which summarize the present understanding of these and other polymer/surfactant systems have been published
[1–4]. However, to our knowledge no studies have been published of the interactions of cationic starch with anionic surfactants. This system is of considerable technical interest due to the use of cationic starch as a binder in, for example, papermaking. In the first paper of this series we described
the surface tensions and phase equilibria in dilute aqueous systems containing cationic starch and anionic surfactants. This paper treats aggregate formation and phase separation mechanisms in the same systems, based on measurements of viscosity and light scattering.

The cationic starch used is completely hydrophilic (it is modified by 2-hydroxy-3-trimethyl-
ammoniumpropyl groups). Hence, the only hydrophobic interactions of importance in the starch/surfactant system are those giving rise to cooperative aggregation of the surfactants into micelles. A consequence of this cooperative interaction in surfactant/polymer systems is the occurrence of a critical association concentration (CAC) well

* Corresponding author.
below the critical micelle concentration (CMC) of the surfactant. Accordingly, polymer/surfactant interactions in dilute solutions have been modeled as a co-operative binding of the surfactant to the polymer. However, as indicated by the lowering of surface tension, marked surfactant/polymer interactions occur well below the CAC. Also, gels are formed in very dilute systems. Another way of describing the interaction, therefore, is to consider it as analogous to an associative interaction between two different polymers (polymer and surfactant micelle) [5].

We suggest that while the strong decrease in surface tension at very low surfactant concentrations is due to formation of surface active complexes by way of counter ion condensation [6], this interaction is not easily detected in viscosity measurements which reflect inter- and intramolecular bonding due to micelle/polymer interactions. Dynamic light scattering is shown to yield insight into the processes leading to phase separation and dissolution.

2. Experimental

2.1. Materials

2.1.1. Cationic starch

The cationic starch (CS) samples (2-hydroxy-3-trimethylammonium-propyl starch) were the same as those described in Ref. [6]. They were synthesized from potato starch by Raisio Chemicals, Raisio, Finland. The nitrogen content was determined by the supplier. Because the starch is oxidized by sodium hypochlorite before cationization, it is depolymerized to a considerable degree. Low molecular-weight impurities were removed by dialyzing against distilled water for seven days, using a Spectrapor (Spectrum Medical Industries Inc.) dialysis membrane with a cut-off of 6–8000. Impurity removal was checked by conductance measurements. Dissolution of the starch was ensured by heating the starch solution in an autoclave for 30 min in at 120°C. The solutions were then filtered through a 3.0 μm membrane. All solutions were prepared at least 24 h before measurements.

The molecular-weight distribution, which is very broad, was estimated by size exclusion chromatography. The mean particle size of the starch was determined by dynamic light scattering [6]. Some properties are given in Table 1.

2.1.2. Surfactants

Sodium dodecyl sulfate (SDS) was analytical grade from Fluka AG. The sample was recrystallized three times from ethanol. Potassium n-octanoate (KOct) was synthesized by neutralizing a solution of octanoic acid (Fluka AG, purum) in ethanol (20% solution) with potassium hydroxide. The soap was recrystallized three times from acetone. Sodium oleate (NaOl) was prepared and recrystallized in the same way by adding sodium hydroxide to an ethanolic solution of oleic acid (Sigma Chemicals, analytical grade). Potassium n-dodecanoate (KDod) (ICN Biochemicals, analytical grade) was purified by recrystallization from acetone. The alkanoate solutions were made slightly alkaline (pH 10.5) by adding sodium or potassium hydroxide. The purity and CMC of all surfactants was verified by measurement of surface tension, which showed no minimum in the concentration range below CMC. The CMCs of the surfactants (SDS: 8.25 mmol dm⁻³; KOct: 345.0 mmol dm⁻³; NaOl: 0.90 mmol dm⁻³; KDod: 16.0 mmol dm⁻³) were in good agreement with those reported in the literature [7].

2.1.3. Other chemicals

The water was ion exchanged and distilled. Its conductivity was 2.0 μS and its surface tension was 71.5 ± 0.5 mN m⁻¹ (T = 298 K). All other

<table>
<thead>
<tr>
<th>Starch</th>
<th>Molecular weight range (g mol⁻¹)</th>
<th>Particle size range (μm)</th>
<th>Degree of substitution (DS)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>0.5–7 x 10⁴</td>
<td>0.01–0.3</td>
<td>0.0014</td>
</tr>
<tr>
<td>N2</td>
<td>0.5–10 x 10⁴</td>
<td>0.01–0.6</td>
<td>0.097</td>
</tr>
<tr>
<td>N3</td>
<td>0.5–9 x 10⁴</td>
<td>0.01–0.5</td>
<td>0.415</td>
</tr>
<tr>
<td>N4</td>
<td>0.4–10 x 10⁴</td>
<td>0.01–0.6</td>
<td>0.772</td>
</tr>
</tbody>
</table>

* Calculated from the nitrogen content.
chemicals were analytical grade and were used without further purification.

2.2. Methods

2.2.1. Viscosity

Viscosities were determined with a computer-controlled Ubbelohde capillary viscometer system (Schott-Geräte, AVS 350). The correction factors of Hagenbach were used to calculate the real efflux times. The viscometer was cleaned using aqua regia, ion-exchanged water and distilled water. The viscometer was immersed in an bath thermostatted to 298.15±0.01 K. The samples were allowed to equilibrate for 10 min in the thermostatic bath before measurements.

Several measurements were performed on each sample. The reproducibility between measurements of efflux times on the same sample was normally of the order of ±0.01 s. At certain surfactant/CS ratios the aggregates formed very mobile flocs, which tended to stick in the capillary. At some surfactant concentrations, bubbles tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements.

The results of the viscosity measurements are presented as reduced viscosity values calculated from:

\[
\eta_{\text{red}} = \frac{(t - t_0)/t}{c}
\]

where \(t\) is the measured efflux time, \(t_0\) is the efflux time of the pure solvent (water), and \(c\) is the weight concentration of the polymer.

2.2.2. Dynamic light scattering (DLS)

DLS measurements were made with a Coulter Instruments N4MD light scattering instrument, equipped with a 4 mW He–Ne laser operating at 632.8 nm and a correlator unit with 80 quasi logarithmically-spaced channels, spanning a timescale of 3072 equivalent linearly spaced channels. Samples were prepared the same way as in viscosity measurements. The temperature of the sample chamber was adjusted to 298.15±0.2 K.

The relationship between the measured second-order correlation function \(g^{(2)}(t)\) and the intensity distribution function \(F(R_{\text{eff}})\) of a sample containing polydisperse spherical particles with effective radii \(R_{\text{eff}}\) in a solvent with viscosity \(\eta\) is given by:

\[
[g^{(2)}(t) - 1]^{1/2} = \int_0^\infty F(R_{\text{eff}}) \exp\left[-(q^2 kT/6\pi\eta)R_{\text{eff}}^2 t\right] dR_{\text{eff}} + \delta
\]

where \(q\) is the wave vector and \(\delta\) is a constant background contribution due to scattering from large impurities or dust [8].

The intensity distribution was evaluated from the measured correlation function using the Contin procedure [9,10]. Due to the very high polydispersity of the samples and the tendency of the starch particles to aggregate, detailed analysis of the scattering function is difficult, in particular taking into account that the Contin method tends to undersmooth at short relaxation times and oversmooth at long relaxation times [11]. This, combined with the fact that using a He–Ne laser the lower range of detection is about 3 nm, led to a situation in which micelles were not detectable. The particle sizes calculated from the distribution function should only be considered as a relative measure of the extent of aggregation without much significance attached to the actual values of the diameters. Because of these inherent uncertainties, only the light scattered at 90° was measured.

2.2.3. Electrophoretic mobility

Electrophoretic mobilities were measured with a Coulter Electronics DELSA 440 laser Doppler electrophoretic light scattering analyzer.

3. Results

3.1. Viscosities

3.1.1. The effect of charge density

Fig. 1 shows the effect of adding surfactant (SDS) on the reduced viscosities of solutions of starches with different charge densities. The viscosities at very low SDS concentrations increase with increasing charge density of the CS (N2<N4). This is to be expected as a result of the increasing repulsion between charged segments in the poly-
The effect of added sodium dodecyl sulfate (SDS) on the reduced viscosity of 0.01 wt.% cationic starch solutions, ionic strength 1.3 mmol dm\(^{-3}\). Degree of substitution of starch: ■, 0.097 (N2); ▲, 0.415 (N3); ○, 0.772 (N4). The dotted lines indicate two-phase systems where the gel phase has separated from solution as colloidal particles or a macroscopic precipitate.

Fig. 2. The effect of added sodium dodecyl sulfate (SDS) on the reduced viscosity of 0.01 wt.% CS (sample N1, degree of substitution 0.0014, ionic strength 1.3 mmol dm\(^{-3}\)).

Fig. 3. The effect of adding surfactants with different chain lengths on the reduced viscosity of 0.01 wt.% solutions of CS sample N4 (degree of substitution 0.772, ionic strength 1.3 mmol dm\(^{-3}\)). ○, KOct; ▼, KDod; ■, NaOl; ▲, SDS.

The viscosities are nearly independent of the surfactant concentration until a sudden drop in viscosity occurs, suggesting that enough surfactant has been added to cause the polymer coils to collapse. The viscosity drops until gel particles are formed. This phase separation can also be observed visually as the separated uncharged gel phase is so highly hydrophobic that it does not remain dispersed in the solution. The added surfactant concentration at which the lowest viscosity level is reached depends on the charge density of the polymer (N2 < N4). When adding excess surfactant the CS/surfactant gel dissolves. At the same time the excess surfactant begins to form free micelles. This results in an increasing viscosity.

No effect of added surfactant was observed for sample N1 (Fig. 2). Thus, there seems to be a minimum charge density below which CS/surfactant interactions are negligibly small.

3.1.2. The effect of the hydrocarbon chain length of the surfactant

Fig. 3 shows the effect of different alkanoates on the reduced viscosity of CS solutions. The sudden viscosity drop occurs at lower concentrations the longer the hydrocarbon chain (NaOl < KDod). The interaction between KOct and CS is apparently quite weak, because the concentration where the drop occurs is not well defined. In all cases, the gel phase separating after the viscosity drop is very hydrophobic. The increase in the viscosity when the gel phase dissolves depends on the CMC, and accordingly on the chain length of the surfactant (NaOl < KDod).
3.1.3. The effect of the end group of the surfactant

Fig. 4 compares the effect of SDS and KDod on the reduced viscosity of CS solutions. The viscosity with KDod is lower than with SDS, which is to be expected due to the higher ionic strength of the KDod solution (whose pH was adjusted to 10.5). There is no qualitative difference between the effect of the two surfactants: the CAC and gel formation occur at roughly the same concentrations of both.

3.1.4. The effect of polyelectrolyte concentration

Fig. 5 shows the effect of the concentration of CS on the reduced viscosity of CS/SDS systems. The behaviour is quite complex. On the one hand, the reduced viscosity of solutions containing very low concentrations of SDS increases when the polyelectrolyte concentration decreases, because the ionic strength of the solution decreases and the electrostatic repulsion between charged groups becomes more effective. This is a well-known general property of polyelectrolytes. On the other hand, the viscosity drop takes place at lower surfactant concentrations the lower the CS concentration. Phase separation occurs at higher surfactant concentration the higher the CS concentration (0.001 wt.% < 0.01 wt.% < 0.1 wt.%); for the lowest CS concentration there is a distinct maximum separated by two minima in the reduced viscosity. The increase in the viscosity when excess surfactant is added occurs at lower surfactant concentrations the lower the concentration of CS.

3.1.5. The effect of electrolyte concentration

Fig. 6 shows the effect of a simple added electrolyte and of an added surfactant (SDS) on the
reduced viscosity of CS solutions. The effects of added salt and SDS are nearly the same. Thus, in order to observe the effect of interaction between the surfactant and CS rather than the effect of increasing ionic strength, it is very important to keep the ionic strength constant when adding a surfactant. Fig. 7 shows the effect of ionic strength on the reduced viscosity of CS/KDoo solutions. The initial reduced viscosity of surfactant-free CS solutions is lower the higher is the ionic strength of the solution. The concentration at which the viscosity drops increases with increasing ionic strength, as does the surfactant concentration, leading to redissolution of the gel.

3.2. Dynamic light scattering

3.2.1. The effect of charge density

Fig. 8 shows how the mean hydrodynamic diameter of the CS particles changes when surfactant (SDS) is added to the solution. In these experiments, the ionic strength was kept constant up to 1.3 mmol dm$^{-3}$ by adding NaCl. As noted in Section 2, only starch particles are seen by the DLS equipment, and not much significance should be attached to the absolute values of the diameters. However, some trends are clear and consistent. The particle size increases with increasing DS of the CS. The size remains constant when low concentrations of SDS are added, up to a rather well-defined concentration at which it drops. This concentration coincides with the concentration at which there is a sudden drop in the reduced viscosity (Fig. 1). There is no effect of adding SDS to the N1 sample (cf. Fig. 2). Thus, both viscosity and light-scattering experiments indicate that the expanded cationic starch particles collapse at a critical concentration of surfactant (the critical association concentration, CAC).

The CAC can also be clearly observed in the

---

1 If the ionic strength of the solution is not kept constant, the hydrodynamic radius of CS particles is reduced even at very low surfactant concentrations because the repulsion between charged segments is screened by the added surfactant ions.
electrophoretic mobility of the starch particles (Fig. 9). While the mobility increases slightly with increasing SDS concentrations (presumably due to the compression of the diffuse double layer around the particles as the ionic strength increases), there is a sudden drop at $\log([SDS]) \approx -3.8$, which coincides with the viscosity drop for the same concentration of CS (Fig. 5). The gel precipitates when the mobility of the particles is $\approx 0$ (Fig. 9).

The CAC and the progress of the association phenomena is also indirectly indicated by an increase in the scattered intensity of up to 10–30 times the initial value. This indicates the occurrence of microscopic inhomogeneities in the system, irrespective of the fact that the discrete particle sizes are decreasing. The inhomogeneities may be due to conformational changes of the polymer upon association, and reversible network formation. The increase in the scattered intensity appears to be of the same kind as is observed, for example, in polyethylene oxide solutions at temperatures a little below the clouding point [12]. The scattering intensity may also increase due to the decreasing net charge of the polyelectrolyte/surfactant complex (and thinning counter-ion layer). The progress of the association is also visually observable as the solutions become slightly turbid.

3.2.2. Gel formation

The separation of a gel phase results in a sudden increase in the size of the CS particles. When excess surfactant is added the aggregates disappear, and the size of the particles is nearly the same as before phase separation. As redissolution proceeds, the net charge of the aggregate becomes more negative (Fig. 9).

The progress of association and redissolution can be clearly followed by the Contin particle-size distribution analysis (Figs. 10(a)–(d)).

Surfactant-free CS contains two particle fractions: a main fraction with particle diameter from 80 to 400 nm, and small fragments which are probably formed during the sodium hypochlorite oxidizing process used before cationization (Fig. 10(a)). Upon association to a gel phase the small starch fragments aggregate (Fig. 10(b)), and when phase separation is complete, the size distribution of the particles is unimodal with a rather broad distribution of sizes (Fig. 10(c)). After redissolution the size of the particles is again bimodal, but the smaller particles are now much larger than at low SDS concentrations (Fig. 10(d)).

3.2.3. The effect of the hydrocarbon chain length of the surfactant

Comparison of NaO1, KDod and KOct (Fig. 11) shows that the CAC, particle aggregation and phase separation all occur at lower concentrations when the surfactant chain length increases. For potassium octanoate, a visually observable formation of the gel phase does not occur, presumably because the hydrocarbon chain is very short.

3.2.4. The effect of the end group of the surfactant

Fig. 12 compares the interactions between starch and surfactants with two different end groups. As was the case for the viscosities, there is no qualitative difference between the effect of SDS and KDod as oppositely charged surfactants in CS solutions. However, the CAC of SDS is lower and the particle size in dilute solutions is higher than the corresponding quantities for KDod: SDS also lowers the surface tension of CS solutions more effectively than KDod [6]. These effects may all be due to the somewhat higher ionic strength of the KDod solutions (ph 10.5).
3.2.5. The effect of polyelectrolyte concentration

Fig. 13 shows the effect of the concentration of CS on the particle sizes. As was to be expected from the viscosity measurements, the initial particle size and the CAC increases as the polyelectrolyte concentration increases. On the other hand, the rise in the average particle diameters characteristic of aggregate formation (and phase separation) clearly occurs at lower concentrations of surfactant, the more dilute the solution of starch.

3.2.6. The effect of the electrolyte concentration

Fig. 14 shows the effect of added electrolyte on the CS(sample N4)/SDS system. The CAC shifts to slightly larger concentrations as the electrolyte concentration increases. Phase separation occurs at lower concentrations when 0.001 M NaCl is added, but shifts to higher surfactant concentrations at higher (0.01–0.1 M) salt concentrations. Phase separation is quite insensitive to electrolyte concentrations in the sense that even in 0.1 M salt concentration the two-phase area is only marginally reduced.

4. Discussion

4.1. General considerations

The main interactions between polyelectrolytes and oppositely charged surfactants are (1) electrostatic interactions, (2) hydrophobic, and (3) solva-
Fig. 11. The effect of adding surfactants with different chain lengths on the mean particle size of 0.01 wt.% solutions of CS sample N4 (degree of substitution 0.772, ionic strength 1.3 mmol dm$^{-3}$). ■, NaOlc; ●, KDod; ▽, KOct.

Fig. 12. The effect of adding surfactants with different end groups but the same hydrocarbon chain length on the mean particle size of 0.01 wt.% solutions of CS sample N4 (degree of substitution 0.772, ionic strength 1.3 mmol dm$^{-3}$). ●, KDod; ■, SDS.

Fig. 13. The effect of adding SDS on the particle size distribution in 0.01 wt.% (■) and 0.1 wt.% (●) solutions of CS sample N4 (degree of substitution 0.772).

Fig. 14. The effect of adding SDS on the mean particle size in 0.01 wt.% solutions of CS sample N4 (degree of substitution 0.772), at different concentrations of added NaCl. NaCl concentrations: ■, No salt; ▽, 1 mmol dm$^{-3}$; ●, 10 mmol dm$^{-3}$; ▲, 100 mmol dm$^{-3}$.

sorption of the polymer and the polar end-groups of the surfactant.

Little is known about the effect of solvation on polymer/surfactant interactions, but the general properties of the CS/surfactant systems can be understood qualitatively by assuming that only hydrophobic and electrostatic interactions are of importance.

The CS does not have any hydrophobic segments, so that while hydrophobic surfactant/
(2) Interactions between the ionic end-groups of the surfactant: for the homologous surfactants the most important molecular parameter affecting these interactions is the size of the hydrocarbon moiety, which determines the packing conditions of the monomers into micellar aggregates.

(3) Interactions between the substituent ionic groups in polyelectrolyte and the ionic end-groups of the surfactant.

(4) The screening effect of added simple electrolyte.

4.2. Polymer charge density

The viscosity and light-scattering measurements show that the dimensions of the polymer coil depend linearly on the charge density of the polymer. The electrostatic repulsion between charged segments increases the dimensions of the polymer coils and leads to a more open conformation, which is seen from the DLS data of very low concentrations of surfactant or surfactant-free CS solutions. Generally, the polymer concentration has a big effect on the viscosity of polyelectrolyte solutions. Normally the viscosity of a polymer solution decreases when the solution is diluted, but with polyelectrolytes the situation is quite complex, because diluting the solution also leads to decreasing counter-ion concentration. This lower counter-ion concentration results in a more open polyelectrolyte conformation, thus increasing viscosity.

The effect of electrolyte concentration on polyelectrolyte conformation is often described in terms of an electrostatic persistence length $P_{el}$. For a wormlike chain, a good approximation of $P_{el}$ is given by:

$$P_{el} = \frac{I_B}{4\kappa^2 b^2 \xi^2}$$  \hspace{1cm} (3)

where

$$I_B = \frac{z^2 e^2}{4\pi \varepsilon_0 \varepsilon_r kT}$$  \hspace{1cm} (4)

is the Bjerrum length at which two electronic charges of magnitude $q$, in a solvent of dielectric constant $\varepsilon_r$, interact with energy $kT$:

$$\kappa^{-1} = \left(8\pi I_B \varepsilon_r\right)^{-1/2}$$  \hspace{1cm} (5)

is the Debye parameter, $b$ is the mean distance between charges along the chain, and the dimensionless charge-density parameter $\xi$ is given by

$$\xi = \frac{I_B}{b}$$  \hspace{1cm} (6)

For starch sample N4, $b \approx 0.52$ and $\xi \approx 1.38$, giving the following theoretical values of $P_{el}$ in a 1:1 electrolyte solution: $C_{salt}$ (0): 150 nm, $C_{salt}$ (1 mM): 34 nm and $C_{salt}$ (10 mM): 3 nm. The values at high ionic strengths are obviously unrealistically small, but the calculations show how sensitive the conformation and hence the viscosity of the starch solutions will be to the electrolyte concentration.

4.3. Critical association concentrations

The point at which a sudden drop in viscosity occurs and the CAC, as indicated by particle size measurements, both decrease with increasing surfactant chain length (Figs. 2 and 8). This dependence of surfactant/CS interactions on the surfactant chain length indicates, as in many other systems [13–15], that the critical association involves co-operative interactions between the hydrocarbon chains. With KOct neither the viscosity measurements or the particle sizes indicate any CS/surfactant interactions. Thus, there is a minimum alkyl chain length below which the formation of free micelles is energetically preferred to association with CS.

The critical concentration of surfactant at which there is a sudden drop in reduced viscosity depends logarithmically on the DS of the starch (Fig. 15). On the other hand, the critical association concentrations determined by surface tension measurements [6] decreases as the DS of the polymer increases. It is also remarkable that there is no significant difference between the CACs of sample N4 (DS = 0.772) and sample N3 (DS = 0.415) when determined from surface-tension curves. The concentrations indicated by surface tensions are
also lower than the concentrations at which the viscosity drops take place. Thus, the latter concentrations do not indicate the minimum surfactant concentration at which marked polymer/surfactant interactions take place. Indeed, one does not expect the viscosity of the solution to be a very sensitive method of detecting association phenomena. It shows only bulk solution effects. Thus, it seems reasonable to assume that the primary interaction involved is surfactant/monomer association, which is seen on the surface tension curves. The charge density of samples N4 and N3 is so high that according to Manning’s theory of ion condensation, the effective charge density of the both samples is the same. At somewhat higher surfactant concentrations, enough surfactant is associated with the polymer that hydrophobic interactions and effective screening of the endgroup repulsion by the polymer leads to the formation of micelles associated with the polymer. The dimensions of the CS/surfactant complex then decrease.

Figs. 1 and 8 show that the viscosity drop and thus the aggregation of the surfactant takes place at higher concentrations the higher the DS of the polymer. Obviously, more surfactant is needed to neutralize the charge of the polymer as the DS increases. The dimensions of the molecules of the polymer may also be of some importance. It is possible that at low polymer charge-density the polymer can more effectively shield the repulsion between surfactant molecules, leading to a lower free energy of aggregate formation.

As seen in Fig. 4, the viscosity drops at lower surfactant (SDS) concentrations the lower the CS concentration. As discussed in Ref. [6], the main driving force for initial surfactant association with the CS is counter-ion condensation, which is primarily dependent on the CS charge density and not on surfactant concentration. Hence, when the polymer concentration decreases, less surfactant is required for the formation of micellar aggregates with the polymer.

The electrophoretic mobilities give the same information as the viscosities. The net charge of the particles begin to decrease at the same surfactant concentration at which the viscosity drops.

The main effect of the electrolyte in polyelectrolyte/surfactant systems is screening of the electrostatic interaction between the polymer and the surfactant. The addition of a simple electrolyte also promotes free micelle formation by screening the electrostatic repulsion between the head groups of the surfactant monomers. Hence in dilute concentrations, adding salt decreases the CAC, but at higher concentrations it also decreases the association and the redissolution. From Fig. 14, which shows the effect of adding different amounts of salt (NaCl) to CS/SDS systems, it can be observed that the association between surfactant micelles and CS coils takes place at lower concentrations when adding more salt. The same effect is also seen in the viscosity curves (Figs. 7(a) and (b)).

The other effect which is detectable is the higher concentration of surfactant required to precipitate the gel when more electrolyte is added. It is clearly seen that the difference between CAC and intermolecular association (gel formation) increases with increasing electrolyte concentration (Fig. 14).

4.4. Phase separation and aggregate size

The size distributions (Figs. 10(a)–(d)) show that the primary aggregation process is the disappearance of the small starch fragments which have associated with the surfactant. When the charge of the CS/surfactant aggregates is almost neutral,
intermolecular binding takes place and phase separation happens.

Phase separation commonly occurs in systems of a polyelectrolyte and an oppositely charged surfactant. It has been shown by Lindman et al. [5] that phase separation is due to the aggregation of surfactant micelles and polyelectrolyte coils. Our results show that phase separation occurs well below the CMC of the pure surfactant when surfactant in excess of the amount equivalent to the polymer charge is added.

Because there are no hydrophobic segments on CS, there is no strong intermolecular network formed when the surfactant binds to the polymer due to charge neutralization. Thus, the viscosity rise at onset of gelation is not as big as is typical for EHEC [16,17] and other hydrophobic polymers [18,19]. The phase diagrams of CS/surfactant systems [5] show that the water content of the gel phase is much lower (50–60%) than in the case of EHEC or other modified cellulosics [20,21]. This indicates that the gel phase in the CS is more hydrophobic, and also that the interactions between polyelectrolyte and surfactant are stronger than in the EHEC systems.

The surfactant concentrations required to cause phase separation increase with the DS of the CS. Also, a certain minimum charge density on the CS is required for phase separation or other detectable interaction between polymer and surfactant. With CS sample N1 (DS = 0.014), no phase separation or other interactions were observed. This is consistent with the notion that primary surfactant/polymer association takes place by counter-ion condensation.

The polymer concentration has the same kind of effect. The lower the polymer concentration, the less surfactant is needed to separate out the gel phase. Phase separation and gel formation occur even in CS solutions as dilute as 0.001 wt.%. Thus, it is clear that both charge neutralization and hydrocarbon chain length play an important role in phase separation and aggregation phenomena.

In the redissolution (which, as noted previously, takes place by a charge reversal mechanism) the biggest aggregates break apart, but the smallest starch fragments are left in the form of aggregates, as is seen in Fig. 10(d). The charge of starch/surfactant aggregates after redissolution is opposite to the original starch particles. When adding much more surfactant than necessary for redissolution, some reaggregation takes place.

Acknowledgements

We thank Raisio Chemicals Oy, Raisio, Finland, for donating the CS samples. This work was supported by the program "Biopolymers" of the Finnish Technology Development Centre (TEKES). The skilful experimental assistance of Ms. Ritta Kivelä in the viscosity and light-scattering measurements is gratefully acknowledged.

References
