Colloid Polym Sci 273:974–983 (1995)
© Steinkopff Verlag 1995

ORIGINAL CONTRIBUTION

J. Merta
P. Stenius

# Interactions between cationic starch and anionic surfactants

## 1. Phase equilibria and surface tensions

Received: 18 November 1994
Accepted: 12 May 1995

Dr. J. Merta (✉) · P. Stenius
Laboratory of Forest Products Chemistry
Department of Forect Products Technology
Helsinki University of Technology
Vuorimiehentie 1A
02150 Espoo, Finland

**Abstract** The surface tensions and the phase equilibria of dilute aqueous cationic starch(CS)/surfactant systems were investigated. The degree of substitution of the CS varied from 0.014 to 0.772. The surfactants investigated were sodium dodecyl sulphate (SDS), potassium octanoate (KOct), potassium dodecanoate (KDod) and sodium oleate (NaOl). The concentrations of CS were 0.001, 0.01 and 0.1 w%.

Critical association concentrations (cac) occur at surfactant concentrations well below the critical micelle concentrations of the surfactants, except for KOct, KDod and NaOl at the lowest CS concentrations investigated (0.001 w%). The surface tensions of CS/surfactant solutions decrease strongly already below the cac. This is attributed to the formation of surface active associates by ion condensation. Associative phase separation of gels formed by CS and surfactant takes place at extremely low concentrations when the surfactant/polymer charge ratio is somewhat larger than 1. The gel is highly viscous and contains 40–60% water, depending on the concentration of electrolyte, the surfactant hydrocarbon chain length and the nature of the polar head of the surfactant.

The concentration at which the phase separation occurs decreases with increasing surfactant chain length and the concentration of simple electrolyte, factors that promote micelle formation. This indicates that the gels are formed by association of CS to surfactant micelles. When surfactant well in excess of charge equivalence is added, the gels dissolve because the CS/surfactant complexes acquire a high charge.

**Key words** Cationic starch – anionic surfactants – surfactant/polymer interactions – surface tension of surfactant solutions – phase equilibria

## Introduction

Recently, several reviews on the structure and dynamics of systems containing water, surfactants and water-soluble polymers have been published [1–4]. Many investigations focus on aggregate structure in dilute solution. Interactions are often described in terms of a cooperative binding of surfactant monomers to the polymer. The strength of the interaction is characterized by a binding constant and a critical association concentration (cac).

The properties of the systems have also been described as resulting from interactions between the polymer and micelles [5]. Thus, it has been shown that the interaction between polyions and ionic micelles leads to an associative phase behaviour analogous to that of polyanion/

polycation systems. In solution, polymer/surfactant interactions promote micelle formation. Thus, the cac often lies far below the critical micelle concentration (cmc) of the surfactant.

For polyion/ionic surfactant systems, the main interaction leading to polymer/micelle association are electrostatic interactions between the surfactant end groups and the polymer and hydrophobic interactions between hydrophobic moieties in the polymer and the hydrocarbon chains of the surfactant. Because the former interactions are screened by electrolyte, the cac usually increases with increasing ionic strength.

However, some surfactant/polymer interaction does occur already well below the cac. This is readily observed as a strong lowering of the surface tension of the solutions at concentrations much lower than the cac.

In this and following papers we present studies of the interactions of cationic starches with anionic surfactants, with emphasis on adsorption in dilute solution, phase behaviour and viscosity. To our knowledge, no studies of this system have been published, in spite of its considerable technical importance. Interactions of surfactants with cationized cellulose were investigated by Goddard et al. [6, 7].

This paper reports on studies of surface tensions and phase equilibria. It is shown that the results can be qualitatively well understood in terms of polycation/polyanion interactions and the formation of surface active complexes by way of counter ion condensation at very low surfactant concentrations.

## Experimental

### Materials

#### *Cationic starch*

The cationic starch was prepared by Raisio Chemicals, Raisio, Finland. It is based on potato starch to which 2-hydroxy-3-trimethylammoniumpropyl groups were grafted. Some properties of the samples are summarized in Table 1. The nitrogen content, from which the degree of substitution was calculated, was determined by the supplier. Low molecular weight impurities were removed by dialysis against distilled water for 7 days, using a dialysis membrane with cut-off $6–8 \cdot 10^3$ (Spectrapor, Spectrum Medical Industries, Inc.). The purity was checked by measuring the conductance of the solution. The molecular weight distribution was determined by size exclusion chromatography (SEC). It is very wide for all samples. The starch is depolymerized to a considerable degree because it is oxidized with sodium hypochlorite before cationization. Therefore, the amylose and amylopectin fractions cannot be separated in the SEC chromatograms. The mean particle size was determined by dynamic light scattering.

**Table 1** Properties of cationic starch samples

| Starch | Molecular weight range ($M_w$)* | Particle size range ($\mu$m)** | Degree of substitution (DS)*** |
|---|---|---|---|
| N1 | $0.5–7*10^4$ | 0.01–0.3 | 0.014 |
| N2 | $0.5–10*10^4$ | 0.01–0.6 | 0.097 |
| N3 | $0.5–9*10^4$ | 0.01–0.5 | 0.415 |
| N4 | $0.4–10*10^4$ | 0.01–0.6 | 0.772 |

* by GPC
** by light scattering
*** as reported by the manufacturer

#### *Surfactants*

Analytical grade sodium dodecyl sulphate (SDS, Fluka Ag.) was recrystallized 3 times from ethanol. Potassium octanoate (KOct) was synthesized by neutralizing a 20% solution of octanoic acid (purum, Fluka Ag) in ethanol with KOH. The soap was recrystallized 3 times from acetone. Sodium oleate was synthesized in the same way by adding NaOH to an ethanolic solution of oleic acid (analytical grade, Sigma Chemicals). Analytical grade potassium dodecanoate (KDod, ICN Biochemicals) was purified by recrystallization 3 times from acetone. The purity of all surfactants was verified by measurement of surface tensions (no minimum in the surface tension at concentrations around the cmc). The critical micelle concentrations determined from the surface tensions (SDS: 8.25 mmol dm$^{-3}$; KOct: 345 mmol dm$^{-3}$; NaOl: 0.90 mmol dm$^{-3}$; KDod: 16.0 mmol dm$^{-3}$) are in good agreement with those reported in literature [8].

#### *Other chemicals*

The water was ion exchanged and distilled. Its conductivity was 2.0 $\mu$S and its surface tension was $(71.5 \pm 0.5)$ mNm$^{-1}$ ($T = 298$ K). All other chemicals were analytical grade. They were used without further purification.

## Methods

*Surface tensions* were measured with a ring tensiometer (Sigma 70, KSV Instruments). In the calculation of surface tensions, the correction factors of Huh and Mason [9] were used. The temperature was 25 °C. In order to suppress the formation of very surface active acid/soap complexes, pH was adjusted to 10.5 with KOH or NaOH. The reproducibility between measurements on different samples was ± 0.5 mNm$^{-1}$. This uncertainty is at least partly due to adsorption of starch of surfactant on the ring. This problem is a well-known weakness of the ring method [10]. The reproducibility between measurements on different samples was ± 1.0 mNm$^{-1}$. This is probably due to the very low concentrations of starch (0.001–0.1 weight %).

### Phase equilibria

Weighed amounts of starch, surfactant and distilled water were equilibrated in tightly closed test tubes by continuous turning over for 7 days in a thermostat at 25 °C. The solution and gel phases were then separated by centrifugation for 30 min at 1600 g. The samples were allowed to equilibrate without stirring for 7 days. Thereafter the phases were separated by careful decantation of the solution. The dry content of the phases was determined by weighing. The amount of nitrogen was determined by Kjeldahl analysis [11]. The amount of surfactant was calculated as the difference between the amount of starch and the total amount of dry matter in the samples.

## Results

### The effect of the charge density

Figure 1 shows how the surface tension of solutions containing starch and surfactant depends on the degree of substitution (i.e., the charge density) of the starch. Sudden changes in the slopes of the surface tension vs surfactant concentration curves (marked by arrows) indicate critical association concentrations. The curve for the starch with the lowest charge density (▼) is similar to the curve that would be observed for a pure surfactant solution. Thus, CS/surfactant interactions cannot be observed below a certain minimum charge density. The measurements of electrophoretic mobility show that the surfactant/polymer complexes formed above the cac are positively charged (Fig. 2).

At surfactant concentrations considerably higher than those corresponding to surfactant/starch charge equivalence, the surface tension rises and passes through a maximum. In these concentration ranges (indicated by dotted curves in Fig. 1) a gel phase containing high concentrations of surfactant and polymer (see below) precipitates from the solution. The precipitation can also be observed visually as a clouding of the sample.

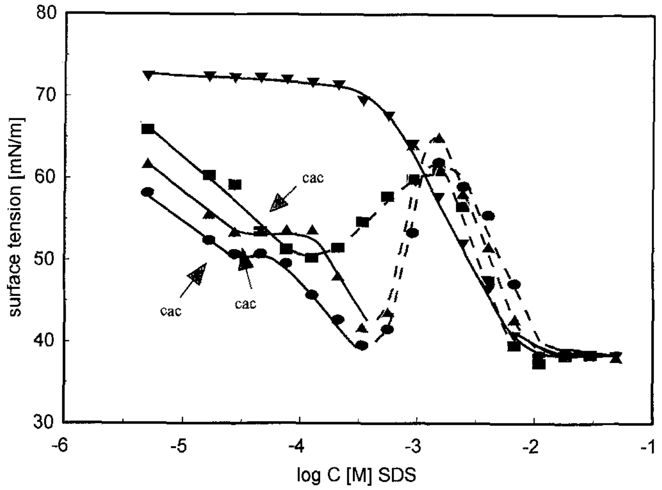


**Fig. 1** Surface tensions of CS/SDS-solutions of cationic starch (CS) having different DS (concentration 0.01 w%) and sodium dodecyl sulphate (SDS). Symbols: (sample/degree of substitution): ▼: N1/0.014; ■: N2/0.097; ▲: N3/0.415; ●: N4/0.772. The two-phase domain is indicated by broken lines. No phase separation was observed for sample N1

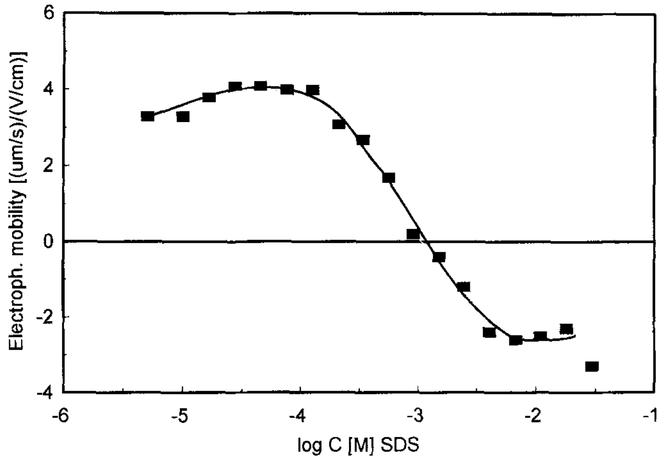


**Fig. 2** Electrophoretic mobilities of aggregates formed in solutions of 0.01 w% CS (sample N4, DS = 0.772). Note that aggregates were detected also in the one-phase areas

Measurements of the electrophoretic mobility show that the gel first separates as positively charged colloidal particles (Fig. 2). These are very difficult to separate from the solution. When more surfactant is added, the particle charge changes from positive to negative. Around the isoelectric point the gel can be readily separated, but the negatively charged particles at higher surfactant concentrations are again very stable. The surfactant concentration range in which phase separation occurs increases with increasing charge density of the starch (N2 < N3 < N4).

When more surfactant is added, the gel phase eventually dissolves and the surface tension becomes almost independent of the surfactant concentration, clearly due to the formation of free micelles in the solution.

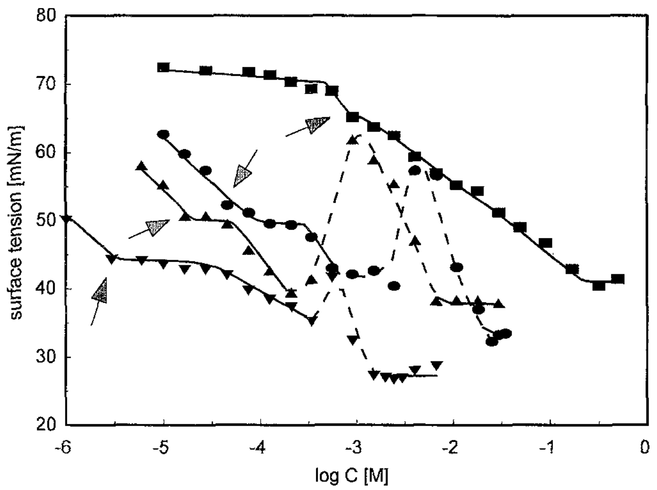
## The effect of the hydrocarbon chain length of the surfactant

Figure 3 shows the surface tension of solutions of surfactant and the CS with the highest charge density (N4). The cac is lower, the longer the hydrocarbon chain of the surfactant (NaOl < KDod < SDS < KOct). The cac of NaOl is difficult to determine because strong interactions occur already at very low concentrations of NaOl. The concentration at which the gel phase separates increases in order NaOl < SDS < KDod. For KOct, it is not possible to visually observe the formation of a gel phase, presumably because very small amounts of gel are formed with this short-chain surfactant. However, when even lower concentrations of starch were used (0.001%) the formation of a gel phase was observed as an increase in the surface tension.

## The effect of polyelectrolyte concentration

Figure 4 shows the effect of the concentration of starch (sample N4) on the surface tension of CS/SDS solution. The cac increases slightly as the concentration of CS increases. On the other hand, phase separation occurs at lower concentrations of surfactant when the concentration of CS decreases. As the CS concentration increases, the effect of phase separation on the surface tensions becomes less marked.

**Fig. 3** Surface tensions of aqueous solutions of cationic starch (CS) (concentrations 0.01 w%) and different surfactants. Symbols: ■: Potassium octanoate (KOct); ●: Potassium dodecanoate (KDod); ▼: Sodium oleate (NaOl); ▲: Sodium dodecyl sulphate (SDS). The two phases are indicated by dotted lines. No phase separation is observed for KOct



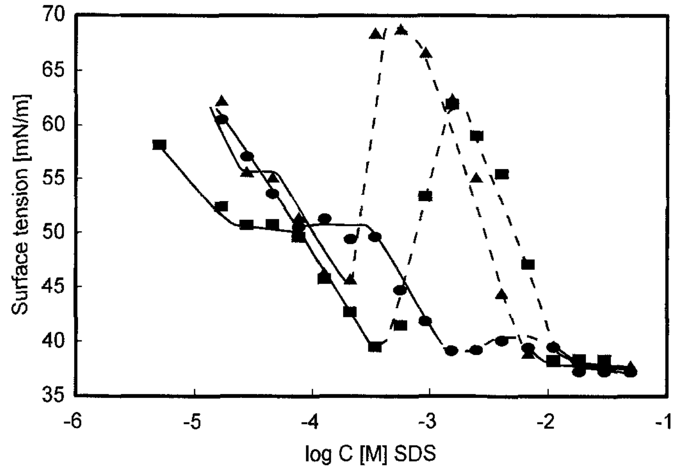


**Fig. 4** Surface tensions of solutions of cationic starch (sample N4, DS = 0.772) and SDS. Concentrations of CS: ▲: 0.001 w%; ■: 0.01 w%; ●: 0.1 w%. The two-phase domain is indicated by dotted lines

## The effect of the concentration of simple salts

Figure 5a shows the effect of added simple electrolyte (NaCl) on the surface tension, $\gamma$ of SDS solutions containing 0.01 weight% CS (sample N4). Without any added salt, in a range below the concentration at which phase separation occurs, $\gamma$ depends on the concentration of SDS, $C_{SDS}$ in same way as the surface tension of SDS solutions containing no CS. The formation of a condensed surface layer is indicated by a steep decrease in $\gamma$ at about the same concentration ($\log C_{SDS} = -4.3$) as in CS free solution.

When 0.001 M NaCl is added, $\gamma$ is lowered by $\approx 10\,\mathrm{mN\,m^{-1}}$ in the lowest concentration range of SDS. The sharp decrease in surface tension occurs at $\log C_{SDS} = -4$. When more NaCl was added at very low $C_{SDS}$, cac is further lowered. For 0.1 M NaCl, no cac can identified. In Fig. 5a, the ionic strength increases as $C_{SDS}$ increases. Figure 5b shows the results when NaCl was added so as to keep the ionic strength constant up to a certain $C_{SDS}$ (see the explanation in the figure text). When the ionic strength increases from 0.001 to 0.002 the surface tension at low $C_{SDS}$ increases. At both ionic strengths, a cac can be identified; its value increases with ionic strength.

The effect of added simple electrolyte and the hydrocarbon chain length of the surfactant is shown for carboxylates in Fig. 3 and in Tables 2 and 3. When KOct is

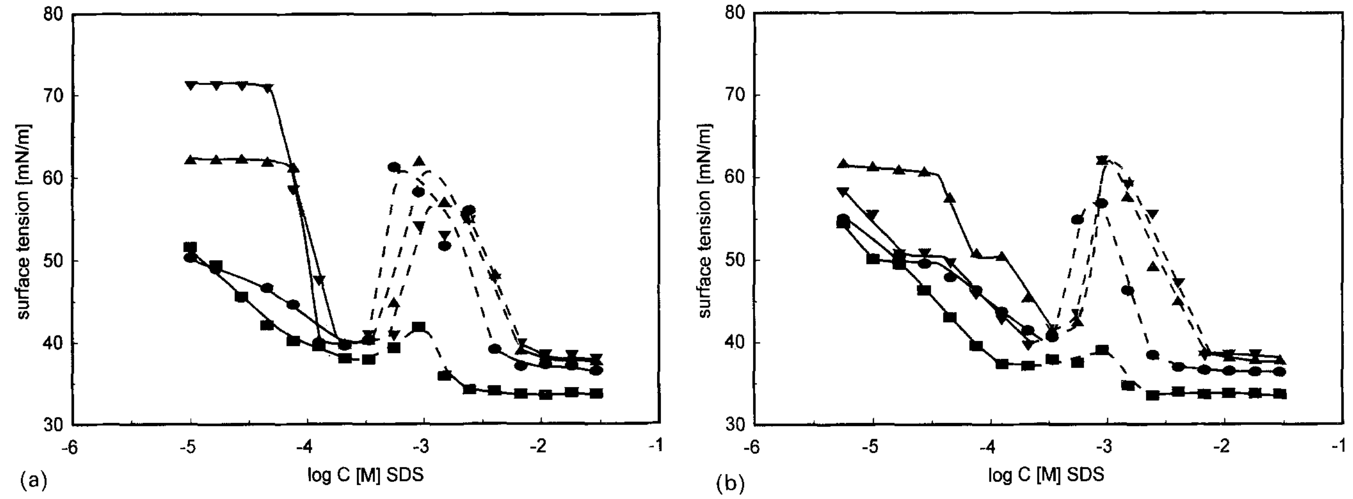


**Fig. 5** The effect of adding NaCl on the surface tensions of solutions of cationic starch (sample N4, DS = 0.772) and SDS. (a) The concentration of NaCl was kept constant. Added NaCl concentrations (mol dm$^{-3}$): ▼: none; ▲: 0.001; ●: 0.01; ■: 0.1. (b) The ionic strength was kept constant up to ▲: 0.001; ●: 0.01; ■: 0.1 mol dm$^{-3}$ by adding NaCl. ▼: no NaCl added

added to 0.01 weight % CS, a cac can be identified in solutions without any added salt (Fig. 3), but the cac disappears when 1 mmol dm$^{-3}$ KCl is added. When the CS concentration is lowered to 0.001 weight %, the formation of a gel phase can be identified (the upper and the lower concentration ranges, Table 2, are uncertain). Gel formation is suppressed when more CS is added (Table 2) and when KCl is added (Table 3).

When the length of the hydrocarbon chain of the carboxylate increases, the cac is lowered (Fig. 3); when salt is added or when the concentration of CS increases the cac increases. The cmc is lowered by adding salt, so that, as has been observed for many other ionic surfactant/polymer systems, the difference between cmc and cac decreases as the salt concentration increases and also when the polymer concentration increases.

Phase separation occurs at lower surfactant concentrations and in a narrower surfactant concentration range as the chain length of the surfactant increases (Fig. 3, Table

**Table 2** Critical association concentrations (cac), lower and upper surfactants concentrations of two-phase area and critical micelle concentrations (cmc) of the pure surfactants in systems of cationic starch (sample N4, DS = 0.772) and different surfactants at 25 °C

| Surfactant | cac mmol dm$^{-3}$ | Lower phase boundary mmol dm$^{-3}$ | Upper phase boundary mmol dm$^{-3}$ | cmc mmol dm$^{-3}$ | log(cmc)–log(cac) |
|---|---|---|---|---|---|
| CS 0.001 w% | | | | | |
| SDS | 0.032 | 0.25 | 7.9 | 8.25 | 2.4 |
| KOct | – | (5.6) | (28) | 345 | |
| KDod | – | 1.0 | 20 | 16 | |
| NaOl | – | 0.028 | 0.79 | 0.90 | |
| CS 0.01 w% | | | | | |
| SDS | 0.032 | 0.50 | 10 | | 2.4 |
| KOct | 0.89 | – | – | | 2.59 |
| KDod | 0.040 | 2.8 | 20 | | 2.60 |
| NaOl | | | | | |
| CS 0.1 w% | | | | | |
| SDS | 0.079 | 0.25 | 16 | | 2.02 |
| KOct | – | – | – | | |
| KDod | 0.063 | 4.0 | 25 | | 2.40 |
| NaOl | 0.010 | 1.6 | 5.0 | | 1.95 |

**Table 3** Critical association concentrations (cac) and lower and upper surfactant concentrations of two-phase area in systems of cationic starch (sample N4, DS = 0.772, concentration 0.01 w%) and different surfactants at 25 °C

| Surfactant/ added electrolyte mmol dm$^{-3}$ | cac mmol dm$^{-3}$ | Lower phase boundary mmol dm$^{-3}$ | Upper phase boundary mmol dm$^{-3}$ |
|---|---|---|---|
| SDS/NaCl | | | |
| No added salt | 0.032 | 0.50 | 10 |
| 1.0 | 0.079 | 0.50 | 10 |
| 10 | 0.010 | 0.35 | 3.6 |
| 100 | – | 0.35 | 2.5 |
| KOct | 0.89 | – | – |
| No added salt | 0.89 | – | – |
| KDod/KCl | | | |
| No added salt | 0.040 | 2.8 | 20 |
| 1.0 | 0.079 | 2.8 | 19 |
| 10.0 | 0.13 | 2.7 | 18 |
| 100 | 0.16 | – | – |
| NaOl/NaCl | | | |
| No added salt | 0.0032 | 0.31 | 1.12 |
| 1.0 | – | – | – |
| 10.0 | 0.0056 | 0.22 | 0.63 |
| 100 | 0.0089 | – | 0.50 |

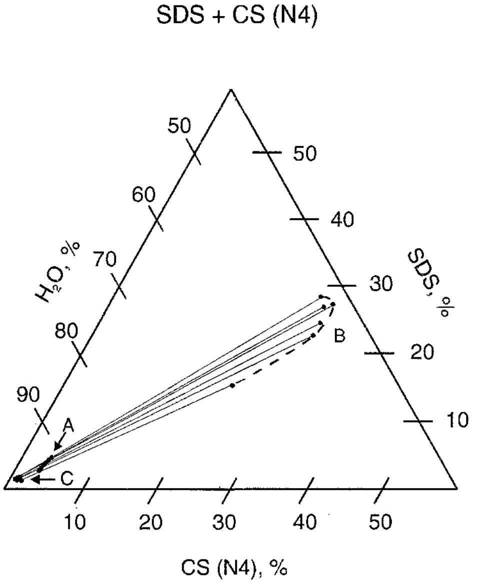


**Fig. 6** Partial phase diagram of the system CS (N4)/SDS/water at 25 °C. Points A indicate the compositions prepared in experiments; points B gives analyzed compositions of the gel phase and points C represent the compositions of the supernatant aqueous phase

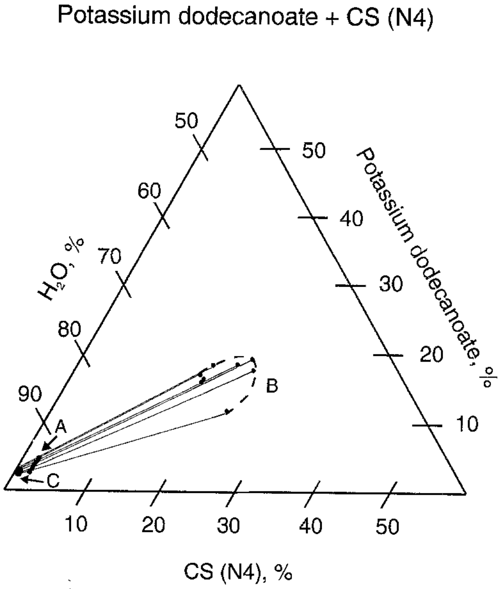


**Fig. 7** Partial phase diagram of the system CS (N4)/KDod/water at 25 °C. Points A indicate the compositions prepared in experiments; points B gives analyzed compositions of the gel phase and points C represent the compositions of the supernatant aqueous phase

2). The effect of adding salt on phase formation is not as well defined as for SDS.

Comparison of the two surfactants with the same chain length (SDS, KDod) shows that the nature of the end group quantitatively affects both the cac and phase separation. The cac of SDS is slightly lower than that of KDod and phase separation occurs at much lower concentrations in SDS solutions than in KDod solutions containing the same amount of CS. Adding salt shifts the phase boundaries in SDS and KDod solutions in the same way, but the effect is much weaker for KDod.

## Phase diagrams

Figures 6–9 show partial phase diagrams for systems consisting of water, the CS with the highest degree of substitution (N4) and SDS, KDod or NaOl. Figures 6 and 7 show that the SDS/CS gel that is in equilibrium with aqueous solution contains considerably less water (45–55%) than the corresponding KDod/CS gel (60–70%). Obviously, the starch/surfactant interactions must be stronger in the SDS/CS gel (as is also indicated by the results given in Fig. 3). The effect of added electrolyte on gel phase formation in the SDS system is shown in Fig. 8. The extent of the two-phase area is decreased, but its general location in the phase diagram does not change significantly. Comparison of Fig. 7 with Fig. 9 shows the effect of increasing the chain length of the surfactant. The water content of the gel formed in equilibrium with aqueous solution by NaOl, CS and water is smaller and the

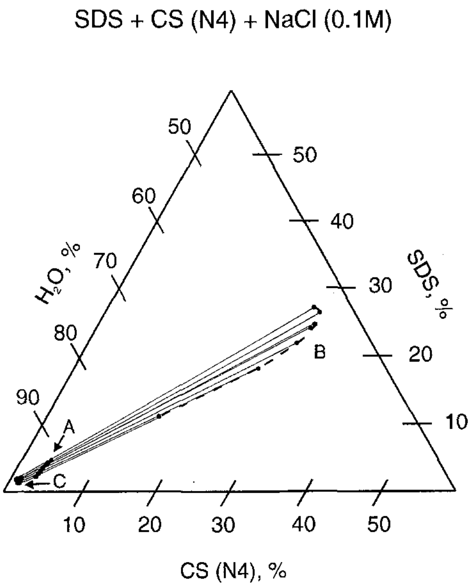


**Fig. 8** Partial phase diagram of the system CS (N4)/SDS/ 0.1 mol dm$^{-3}$ NaCl at 25 °C. Points A indicate the compositions prepared in experiments; points B gives analyzed compositions of the gel phase and points C represent the compositions of the supernatant aqueous phase

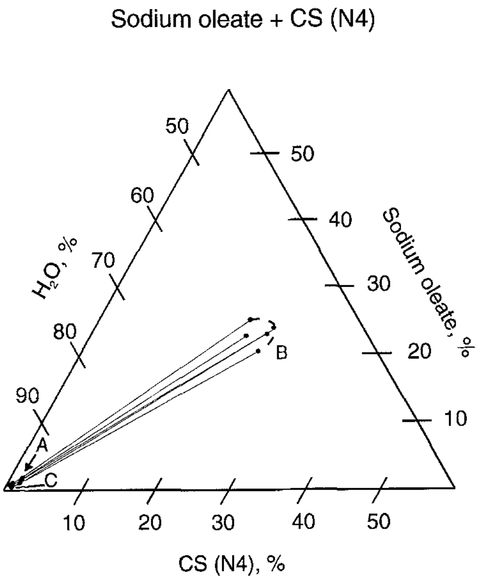


**Fig. 9** Partial phase diagram of the system CS (N4)/NaOl/water at 25 °C. Points A indicate the compositions prepared in experiments; points B gives analyzed compositions of the gel phase and points C represent the compositions of the supernatant aqueous phase

amount of the surfactant is larger than in the corresponding KDod/CS/water gels. It should be noted that the restriction in the mobility of the hydrocarbon chain induced by the double bond in the oleate may also affect the extent to which the gel swells with water.

## Discussion

### General considerations

As has been established in several earlier studies, the main forces governing surfactant/polymer interactions and aggregate formation in ionic systems are i) the entropy change associated with the formation of large aggregates, ii) electrostatic interactions (due to the ionic groups in the polymer and the ionic heads of the surfactant), iii) solvation of the polar end-groups of the surfactant and of the polymer, and iv) hydrophobic interactions (due to hydrophobic moieties in surfactant and in the polymer).

There are no hydrophobic moieties in the cationic starch. Hence, it can be assumed that hydrophobic surfactant/polymer interactions, which are prominent in many systems containing modified nonionic polysaccharides, are unimportant.

The electrostatic interactions can, schematically, be divided into:

1) Interactions between the ionic groups on the polymer. These strongly affect the conformation of the free polymer coil in solution. The most important molecular parameter governing these interactions is the charge density (DS) of the polyion.

2) Interactions between the ionic heads of the surfactant. These interactions oppose the formation of micellar aggregates. For a homologous series of surfactants, the most important molecular parameter affecting these interactions is the size and structure of the hydrocarbon moiety, which determines the packing conditions of the monomers into micellar aggregates and the balance between aggregation-promoting hydrophobic interactions and electrostatic repulsion.

3) Interactions between the ionic groups in the polyelectrolyte and the end-groups of the surfactant. A useful approach is to consider this as analogous to the interaction between two polymers of opposite charge: one "polymer" is formed when the surfactant monomers form micellar aggregates, the other polymer is the added polyelectrolyte [5].

Finally, one has to consider the screening effect of added simple electrolyte on all electrostatic interactions.

### Adsorption at the air/liquid interface

As shown by Fig. 5, the surface tension of CS/SDS solutions with very low SDS concentrations ($< 0.05$ mmol dm$^{-3}$) drops considerably ($\approx 10$ mN/m) when a small amount of simple electrolyte (1 mmol dm$^{-3}$ NaCl) is added.

The CS alone is not markedly surface active, as shown by Fig. 5a (no simple electrolyte added). The activity of the SDS monomers is increased and the cmc of SDS lowered when simple electrolyte is added. However, with a salt addition as low as 1 mmol dm$^{-3}$ this effect should be small, as is indeed confirmed by the small effect of NaCl on the surface tensions at higher $C_{\mathrm{SDS}}$. Neither can the lowering of the surface tension be explained by cooperative interaction of the surfactant with the polyelectrolyte. This interaction manifests itself in the occurrence of a cac, which increases as electrolyte is added.

A possible explanation for the observed lowering of the surface tension is offered by ion condensation and the sensitivity of polyelectrolyte conformations to the electrolyte concentration. The effect on conformation is often described in terms of an electrostatic persistence length $P_{\mathrm{el}}$. For a wormlike chain, $P_{\mathrm{el}}$ to a good approximation is given by

$$P_{\mathrm{el}} = \frac{l_{\mathrm{B}}}{4\kappa^2 b^2 \xi^2}\,, \tag{1}$$

where

$$l_{\mathrm{B}} = \frac{z^2 e^2}{4\pi\varepsilon_0 \varepsilon k T} \tag{2}$$

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

$$\kappa^{-1} = (8\pi l_{\mathrm{B}} c_{\mathrm{s}})^{-1/2} \tag{3}$$

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

$$\xi = \frac{l_{\mathrm{B}}}{b}\,. \tag{4}$$

According to the Manning theory of ion condensation on linear polyelectrolytes [12], when $\xi$ exceeds a critical value, some ions will remain attached to the polyion even at infinite dilution, thereby effectively reducing its charge. For a polyion with monovalent charged groups immersed in an 1:1 – electrolyte, the critical value of $\xi$ is 1, corresponding to $b = 0.702$ nm. For starch sample N4, $b \approx 0.52$ and $\xi \approx 1.38$.

The persistence length is strongly affected by electrolyte concentration. In a 0.01% solution of CS N4 the concentration of free ions will be $\approx 0.3$ mmol dm$^{-3}$, which using Eq. (1) gives $P_{\mathrm{el}} \approx 150$ nm. Adding 1 mmol dm$^{-3}$ NaCl reduces $P_{\mathrm{el}}$ to $\approx 34$ nm; in 10 mmol dm$^{-3}$ NaCl $P_{\mathrm{el}} \approx 3$ nm.

It can be concluded that ion condensation takes place on the CS N4 starch and that the conformation of the molecule shrinks very rapidly when the concentration of added electrolyte increases. The condensation of counter ions would also apply to monomer surfactant counter ions, so that there would be an enhancement of the hydrophobic moieties of surfactant close to the polyelectrolyte chain even at surfactant concentrations below the cac. It seems reasonable that these two effects would lead to the formation of amphiphilic polymer/surfactant complexes that adsorb at air/liquid interface and lower the surface tension, as observed in Fig. 5a.

## Critical association concentrations

Figure 3 and Table 2 show that the log(cac) decreases linearly with increasing chain length. Thus the tendency of the surfactant to form micellar aggregates associated with the polymer increases as the size of the hydrophobic moiety increases. No cac can be observed for KOct. Thus, if the hydrocarbon chain is very short, the formation of free micelles is energetically preferred to those bound to CS.

The polymer concentration only slightly affects the cac. Indeed, the effect is about the same as the effect of increasing the ionic strength of the solution by adding a corresponding amount of simple electrolyte.

Adding simple electrolyte screens the electrostatic interaction between the polymer and the surfactant as well as the repulsion between the ionic groups of the CS. Hence, the cac should increase with increasing electrolyte concentration, as is indeed confirmed by the results shown in Table 3 and Figs. 4 and 5. Added electrolyte also screens the repulsion between the head groups of the surfactant ions, so that the cmc is lowered.

The cac is lowered when the linear charge density of the CS increases (Fig. 1), i.e. CS with higher charge density screens the repulsion between the surfactant end groups more effectively.

## Phase separation and redissolution

### *Phase separation*

Phase separation is a general feature of systems containing a polyelectrolyte and a surfactant of opposite charge. The formation of a second phase shows up as a hump in the surface tensions (Figs. 1, 3–5). Actually, this is a very simple and sensitive way to detect phase separation. Presumably the measured surface tensions in the two-phase area are those of the aqueous solution, which becomes depleted in surfactant as the gel precipitates. When additional surfactant is added, the solution concentration of surfactant increases, the system eventually becomes homogeneous and the surface tension approaches values characteristic for the pure surfactant solution above the cmc.

It was shown by Lindman et al. [5] that the occurrence of a critical association concentration and phase separation can be described in terms of the association of surfactant micelles with polymer coils. Phase separation occurs when binding of surfactant micelles to the polyelectrolyte reduces the total charge of the complexes to a low value.

The importance of electrostatic interactions is obvious. Firstly, the higher the DS of the CS, the higher is the surfactant concentration required to precipitate the gel phase. Secondly, phase separation or other surfactant/polymer interactions cannot be detected when the DS is very low (no interactions were observed for sample N1 with DS = 0.0014). Thirdly, the lower the polymer concentration, the less surfactant is needed to precipitate the gel phase, which is formed even the CS concentration is as low as 0.001%.

However, our results show that phase separation does not coincide with the surfactant/polymer ratio corresponding to charge equivalence. Actually, it takes place when an excess of surfactant has been added (but well below the cmc of the pure surfactant). When the surfactant chain increases, the phase separation concentration decreases, just as the cac and the cmc of the surfactant (Tables 2 and 3). Phase separation does not occur if the surfactant chain is very short (KOct). Clearly, the cooperative hydrophobic interactions between the surfactant alkyl chains also affect phase separation. This constitutes strong evidence that the description of surfactant/polymer complexation as a polymer/micelle interaction is adequate.

The electrolyte concentration does not affect phase separation as markedly as in other systems of anionic polyelectrolyte and cationic surfactants [13, 14]. The surfactant/polymer interaction is weakened when electrolyte is added (the cac increases, Table 3). On the other hand, small amounts of simple electrolyte (1–10 mmol dm$^{-3}$) slightly decrease the lower phase boundary, and the cmc of the surfactant. Higher electrolyte concentrations (0.1 mol dm$^{-3}$) reduce the width of the two-phase area, but phase separation still occurs. It can be concluded that phase separation is more strongly affected by the lowering of the electrostatic repulsion between the surfactant end groups, which promotes micelle formation, than by the weakening of polyelectrolyte/micelle interactions.

### *Dissolution of precipitated CS/surfactant*

Two mechanisms by which polymer/surfactant complexes could be dissolved have been suggested. One is that redissolution is due to a decreased binding of the surfactant to the polymer because it is preferentially bound in free micelles. This would generally require surfactant concentrations much higher than cmc. Another mechanism is that surfactant binding increases to the extent that the complexes become negatively charged. For example, phases formed by cationic cellulose and surfactant dissolve in this way [7].

Measurements of the electrophoretic mobilities of the CS/surfactant particles (Fig. 2) show that the particles become negatively charged when sufficient surfactant is added. Concomitantly, the gel phase dissolves. At low CS concentrations, dissolution takes place at surfactant concentrations ≈ the cmc of the pure surfactant. These observations indicate that the phases dissolve by the charge reversal mechanism. The charge density of the CS affects redissolution. The gel formed by surfactants with the CS with the highest DS (N4) never dissolve completely. This behaviour was also observed for other systems were the phases dissolve by the charge reversal mechanism [7].

### *Phase diagrams*

Although the CS/surfactant/water/simple electrolyte system is actually a four-component system, useful descriptions of the phase behaviour are obtained by plotting three-component diagrams in which it is assumed that the added simple electrolyte forms one component with water. This was done in Figs. 6–9. The phase diagrams are similar to those reported by Thalberg et al. [15] for poly(N,N-dimethyl-3,4-ethylene pyrrolidonium chloride), (PDADMAC) and anionic surfactants. Thalberg et al. [16] were able to theoretically predict the shapes of their phase diagrams by applying the Flory–Huggins theory of the behaviour of polymers in solution [17]. In the model, the surfactant is regarded as another polyelectrolyte. The complex nature of cationic starch makes quantitative calculations for the CS containing systems difficult. However, it is obvious that they qualitatively behave in the same way as the systems described in ref. [16].

Qualitatively applying the concepts of the model used by Thalberg et al., the following observations can be made. It is very likely that association in CS/surfactant systems takes place between the CS and aggregated surfactant monomers. The gel phase has a low water content. Hence, the interaction between CS and anionic surfactants must be much stronger than the interactions between anionic polyelectrolytes and cationic surfactants. This agrees with earlier observations [18, 19]. The reason is not fully understood, but the small size of the polar head of anionic surfactants may be of importance [20].

The importance of the polar head is illustrated by comparison of the SDS/CS systems with the KDod/CS systems. The number of carbon atoms in these surfactants is equal, but the maximum water content of the gel formed by CS and KDod is considerably higher than that of the CS/SDS gels. Although the difference may be partially due to the different counter ions, it also indicates that starch/polar head group interactions are stronger in the CS/SDS system.

When the length of the hydrocarbon chain increases, the cac and the surfactant concentration at the lower phase boundary decreases (Table 2). The maximum water contents of the gels formed by CS (N4) with KDod and NaOl also indicates somewhat stronger interactions in the system containing the surfactant with the longer chain.

Addition of 0.1 mol dm$^{-3}$ NaCl to the SDS/CS (N4)/water system does not induce significant changes in the phase behaviour. This is also indicative of the highly cooperative nature of the CS/anionic surfactant interactions.

Very stiff gels are formed by systems containing a little more surfactant than the amount equivalent to the charge on the CS. The viscosity decreases strongly when slightly more or slightly less surfactant is used. The effect of added electrolyte on the stiffness of the gel phase is weak. Studies of these effects are expected to give additional insight into the structure of the gels and will be reported in forthcoming papers.

**Acknowledgements** This work was supported by the program "Biopolymers" of the Finnish Technology Development Centre (TEKES). The skillful experimental assistance of Ms. Ritva Kivelä in the surface tension measurements is gratefully acknowledged. We thank Raisio Chemicals Oy, Raisio, Finland for donating the CS samples.

---

## References

1. Goddard ED, Ananthapadmanadhan KP (1993) (eds) Interactions of Surfactants with Polymers and Proteins, CRC Press
2. Hayakawa K, Kwak JCT (1991) In: Rubingh DN, Holland PM (eds) Cationic Surfactants. Marcel Dekker, New York, 2nd ed
3. Saito S (1991) In: Schick MJ (ed) Nonionic Surfactants. Marcel Dekker, New York, p 189
4. Robb ID (1981) In: Lucassen-Reynders E (ed) Anionic Surfactants – Physical Chemistry of Surfactant Action, Surfactant Sci Ser, Vol 11, Marcel Dekker, New York, Chap 3
5. Lindman B, Piculell L (1992) Adv Coll Interface Sci 41:149
6. Goddard ED, Hannan RB (1976) J Colloid Interface Sci 55:73
7. Goddard ED, Hannan RB (1977) J Am Oil Chem Soc 54:561
8. Mukerjee P, Mysels K (1971) Critical Micelle Concentrations of Aqueous Surfactant Systems, NSRDS-NBS 36. National Bureau of Standards, Washington
9. Huh C, Mason SG (1975) Colloid Polymer Sci 253:566
10. Simister EA, Thomas RK, Penfold J, Aveyard R, Blinks BP, Cooper P, Fletcher PDI, Lu JR, Sokolowski A (1992) J Phys Chem 96:1383
11. Bradstreet RB (1965) The Kjeldahl Method for Organic Nitrogen, Academic Press, New York
12. Manning GS (1978) Q Rev Biophys 11:179
13. Hayakawa K, Kwak JCT (1983) Macromolecules 16:1642
14. Thalberg K, Lindman B, Karström G (1991) J Phys Chem 95:6004
15. Thalberg K, Lindman B (1991) Langmuir 7:277
16. Flory PJ (1953) Principles of polymer chemistry, Cornell University Press; Ithaca, New York
17. Thalberg K, Lindman B, Karlström G (1990) J Phys Chem 94:4289
18. Goddard ED (1986) Colloids Surf 19:301
19. Thalberg K, Lindman B, Bergfeldt K (1991) Langmuir 7:2893
20. Shirahama K, Himuro A, Takisawa N (1987) Colloid Polymer Sci 265:96