



Interactions between cationic starch and mixed anionic surfactants

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Abstract

The interactions of cationic starch (CS, degree of substitution=0.8)/mixed anionic surfactant/water systems were investigated. The surfactants investigated were sodium dodecyl sulphate (SDS), sodium octanoate (NaOct), sodium decanoate (NaDe), sodium dodecanoate (NaDod), sodium oleate (NaOl) and sodium erucate (NaEr). The concentration of CS varied from 0.001 to 10 wt.%. The effect of mixing on the micellisation of the binary surfactant solutions can be described to a good approximation by taking into account only the effects of the volume difference between the hydrocarbon chains. Mixed micelle formation on CS depends on the chain-length difference in quite the same way as for free mixed micelles. Aggregation of the mixed micelles of the surfactants and the polymer coils produces a gel-like complex phase. The water content of the gel phase in equilibrium with aqueous solution increases when the chain-length difference between the two surfactants increases. The more surface-active component is strongly enriched in the polymer complexes and gels. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many investigations of polymer/surfactant interactions in aqueous systems have focussed on aggregate structures in dilute solutions. The general picture emerging from these studies (for reviews, see Refs. [1-4]) is that the surfactant molecules form micelles or micelle-like clusters when associating with the polymer chains. Another general feature of aqueous systems which contain polyions and oppositely charged surfactants is the separation of insoluble complexes when the amounts of polyion and surfactant roughly correspond to charge equivalence. In most cases, the separated phase is a highly viscous gel containing 60-80%

water. It is often quite easy to separate the gel from the solution phase.

This paper is one in a series of studies of cationic starch and anionic surfactants. In previous papers we described the interactions in aqueous solutions, the formation of a complex phase [5,6] and the rheological properties of these systems [7]. The interactions of surfactants with cationized cellulose and the rheology of the complex phase was investigated by Goddard and Hannan [8,9], but to our knowledge these are the first reported investigations of cationic starch/anionic surfactant systems. In this paper we discuss the interactions in systems of cationic starch (CS) and anionic surfactant mixtures. Very few observations of the properties of polyelectrolyte/mixed surfactant systems have hitherto been published.

A general characteristic of these systems is that

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CS interacts with the surfactant mixtures in a similar way as with a single surfactant, i.e. by associating with mixed micelles. The composition of mixed micelles in solution depends on the relative activities of their components, but the more surface-active component is usually strongly enriched in the micelles. The compositions of the CS/surfactant complexes behave in the same way. The hydrophobicity of the complex phase is governed by the hydrophobicity of the long-chain surfactant. However, even a small fraction of an added short-chain component markedly reduces the viscosity of the gel.

2. Experimental

2.1. Materials

2.1.1. Cationic starch

The cationic starch (CS) (2-hydroxy-3-trimethylammonium-propyl starch), was similar to those described in Refs. [5–7], except that the highest degree of substitution (DS) was (0.80). The product was synthesized by Raisio Chemicals (Raisio, Finland) from potato starch. The DS was calculated from the nitrogen content. The starch was depolymerized by sodium hypochlorite before cationization. Details of the oxidation process are given in Ref. [10].

The starch was purified by filtration in a tangential flow ultrafiltration system (Filtron Technology Corporation, Minisette). A membrane with a cut-off 8000 was used. The starch was dissolved by heating the starch/water mixture in an autoclave for 30 min at 120°C. All solutions were prepared at least 24 h before measurement were performed.

2.1.2. Surfactants

All alkanates (sodium octanoate, $C_7H_{15}COONa$ (NaOct); sodium decanoate, $C_9H_{19}COONa$ (NaDe); sodium dodecanoate, $C_{11}H_{23}COONa$, (NaDod); sodium oleate (sodium *cis*-9-octadecenoate), $C_9H_{18}=C_8H_{15}COONa$ (NaOl); sodium erucate (sodium *cis*-13-docosenoate), $C_9H_{18}=C_{12}H_{23}COONa$ (NaEr)) were synthesized by neutralizing the corresponding acid in an alcoholic solution with sodium hydroxide.

The salts were purified by recrystallization from acetone.

2.1.3. Other chemicals

The water used was ion-exchanged and distilled. All other chemicals were analytical grade and were used without further purification.

2.2. Methods

2.2.1. Surface tension

Surface tension was measured with a ring tensiometer (Sigma 70, KSV Instruments). In the calculation of surface tension, the correction factors of Huh and Mason [11] were used. The temperature was 298 or 333 K, depending on the Krafft point of the surfactants used. Thus, sodium erucate solutions were investigated at 333 K, while all others were investigated at 298 K. The formation of very surface-active acid/soap complexes was suppressed by adjusting the pH to 10.5 with NaOH. The reproducibility between measurements on the same sample was $\pm 0.5 \text{ mN m}^{-1}$. This uncertainty is partly due to the adsorption of starch on the surfactant on the ring. This problem is a well-known weakness of the ring method [12]. The reproducibility between measurements on different samples was $\pm 1.0 \text{ mN m}^{-1}$. This was probably due to the very low concentrations of starch (0.01 wt.%).

2.2.2. 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 thermostated to $298.15 \pm 0.01 \text{ K}$ or $333.15 \pm 0.01 \text{ K}$. The samples were allowed to equilibrate for 10 min in the thermostatic bath before measurements. The reproducibility between measurements of efflux times on the same sample was usually of the order of $\pm 0.01 \text{ s}$. At certain surfactant/CS ratios the aggregates formed very loose 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.

2.2.3. Phase equilibria

Weighed amounts of starch, surfactants and distilled water were equilibrated in tightly closed test tubes by continuous turning for seven days in a thermostat at 298 K. The solution and gel phases were then separated by centrifugation for 30 min at 1600 g. The centrifuged samples were allowed to equilibrate without stirring for seven 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 starch was determined by Kjeldahl analysis of the amount of nitrogen [13]. The amount of surfactant was calculated as the difference between the amount of starch and the total amount of dry matter in the samples. The composition and amount of surfactant in the supernatant phase was determined by a standard gas chromatographic method of carboxylic acid analysis.

3. Results

3.1. Micellisation in mixed surfactant systems

Fig. 1 shows the CMCs of sodium oleate/sodium decanoate mixtures as a function of the mole fraction of sodium decanoate (NaDe) in the mix-

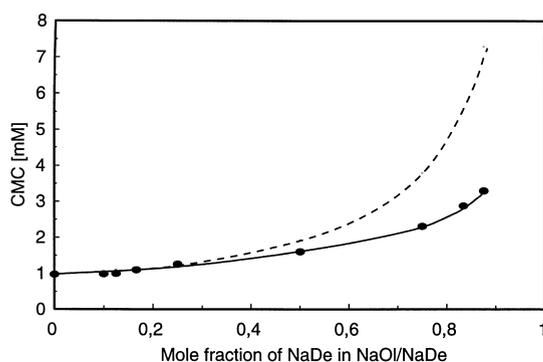


Fig. 1. The CMC of a sodium oleate (NaOl)/sodium decanoate (NaDe) aqueous solution as a function of the mole fraction of the short-chain surfactant (NaDe). Dashed line: ideal solution, circles: experimental results.

ture. The CMCs were determined from surface tension. The dashed line represents the CMC predicted by the theory of ideal mixing (see below). It can be seen immediately that the measured CMC values deviate slightly negatively from the ideal mixing curve, but the CMCs of NaOl/NaDe mixtures are described quite well by the ideal mixing model. Several other surfactant combinations were also investigated. The results are given in Table 1.

3.2. Interactions between cationic starch and surfactant mixtures

3.2.1. Mole ratio of surfactants with different carbon chain lengths

Fig. 2 shows the surface tension of solutions of NaOl and NaOl/NaDe mixtures in 0.01 wt.% starch solutions as a function of the surfactant concentration. Critical association concentrations (CAC) are indicated by sudden changes in the slopes of the curves. When part of the NaOl is replaced by NaDe, the CAC 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 Figs. 2 and 3. Phase separation takes place at higher surfactant concentrations when the fraction of NaDe increases (Fig. 3). Increasing the mole fraction of NaDe above 0.83 does not significantly affect the CAC, but the two-phase area extends to higher concentrations.

The CS/surfactant complex becomes negatively charged [5] and redissolution of the gel phase takes place at the same surfactant concentrations, indicating that an excess of surfactant associates with the polymer. In the presence of a large excess of surfactant, the surface tension changes only slowly with concentration due to the formation of free surfactant micelles in the solution. The CMC increases as the fraction of NaDe increases, and is always significantly higher than for pure NaOl.

Fig. 3 shows the effect of adding of a surfactant

Table 1

Critical micelle concentrations of binary surfactant mixtures (NaOl=sodium oleate, NaDe=sodium decanoate, NaEr=sodium erucate, NaDo=sodium dodecanoate, SDS=sodium dodecyl sulphate)

Mole fraction (α_1) of second surfactant	Critical micelle concentration (mmol dm ⁻³)				
	NaOl/NaDe	NaEr/NaOl ^a	NaEr/NaDe ^a	NaDo/NaDe	SDS/NaDe
0	0.98	0.071	0.071	25.0	8.32
0.17	1.10	0.074	0.081	28.2	9.75
0.25	1.26	0.090	0.092	30.1	10.5
0.50	1.60	0.128	0.122	39.6	15.0
0.75	2.32	0.212	0.236	52.7	24.4
0.83	3.03	0.296	0.406	62.3	32.2
0.91	3.67	0.403	–	73.2	–
1	95.5	0.993	96.7	95.5	95.5

^aMeasured at 333 K. All other CMCs were measured at 298 K.

mixture on the reduced viscosity of a CS solution. Initially, the viscosity remains nearly constant. However, in all curves there is a sudden drop which indicates that sufficient surfactant has been added to cause the polymer coils to collapse. A viscosity minimum occurs when the polymer and the surfactant aggregate to form gel-like particles. Thus the gel does not increase the viscosity of the system, although it has a very high viscosity itself. This is simply because the gel separates very efficiently from the system, in practice due to adsorption of the gel at the surface of the measuring bottles. When surfactant is added in excess of charge neutralization, the CS/surfactant complex

begins to dissolve. At 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 NaOl/NaDe molar ratio is decreased. The viscosity minimum due to charge neutralization also occurs at a higher surfactant concentration than with pure NaOl.

3.2.2. The effect of the chain length of the shorter-chain surfactant

Fig. 4 shows the surface tension when a mixture of NaOl and shorter-chain surfactant is added (1:1

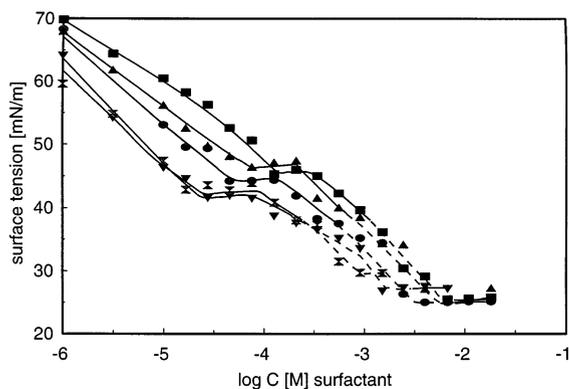


Fig. 2. Surface tensions of solutions of cationic starch (0.01 wt.%, DS=0.80) and NaOl/NaDe mixture. The mole ratios of the surfactants were 1:1 (●), 3:1 (⊗), 1:0 (▼), 1:3 (▲) and 1:5 (■). The two-phase domain is indicated by the dotted line.

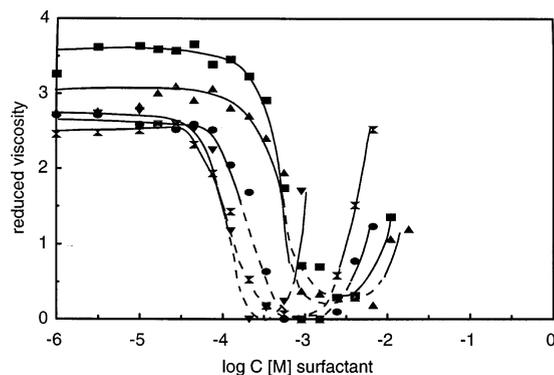


Fig. 3. Reduced viscosities of solutions of cationic starch (0.01 wt.%, DS=0.80) and NaOl/NaDe mixture. The molar ratios of the surfactants were 1:0 (▼), 3:1 (⊗), 1:1 (●), 1:3 (▲) and 1:5 (■). The two-phase domain is indicated by the dotted line.

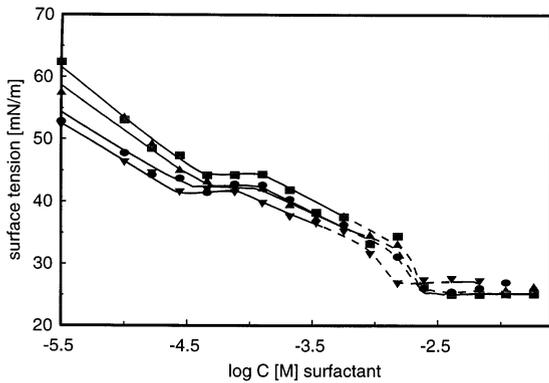


Fig. 4. Surface tension of solutions of cationic starch (0.01 wt.%, DS=0.80) and NaOl/second surfactant mixtures. The surfactants were NaOl (▼), NaOl/NaDod (●), NaOl/NaDe (▲) and NaOl/NaOct (■). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The two-phase domain is indicated by the dotted line.

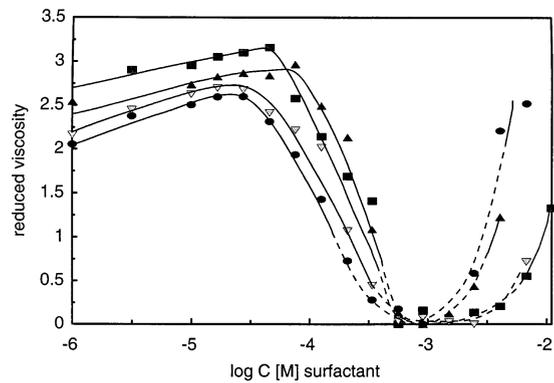


Fig. 5. Reduced viscosities of solutions of cationic starch (0.01 wt.%, DS=0.80) and NaOl/second surfactant mixtures. The surfactants were NaOl (●), NaOl/NaDod (▼), NaOl/NaDe (■) and NaOl/NaOct (▲). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The two-phase domain is indicated by the dotted line.

mole ratio) at constant CS concentration. Although the effect is not very marked, the CAC is always higher than for pure NaOl. The shift decreases when the chain length of the second surfactant increases. The concentration at which the gel phase separates increases in the order NaOl < NaDod < NaDe < NaOct. Redissolution, which is not complete with this highly charged CS (DS=0.80), also takes place at a slightly higher concentration the shorter is the chain length of the second surfactant.

Fig. 5 shows the reduced viscosity of CS solutions containing different surfactant mixtures. The viscosity drop occurs at lower concentrations as the hydrocarbon chain length of the second surfactant is increased. Thus, the interaction depends markedly on the surface activities of the surfactants. The viscosity increase when excess surfactant is added depends on the CMC of the surfactant mixture, and accordingly on the chain length of the second surfactant.

3.3. Phase equilibria

Partial phase diagrams for systems of CS, water and NaOl/NaDe mixtures are shown in Fig. 6. In principle, four component phase diagrams should be used for a full description of these systems. However, for our purposes, sufficient information

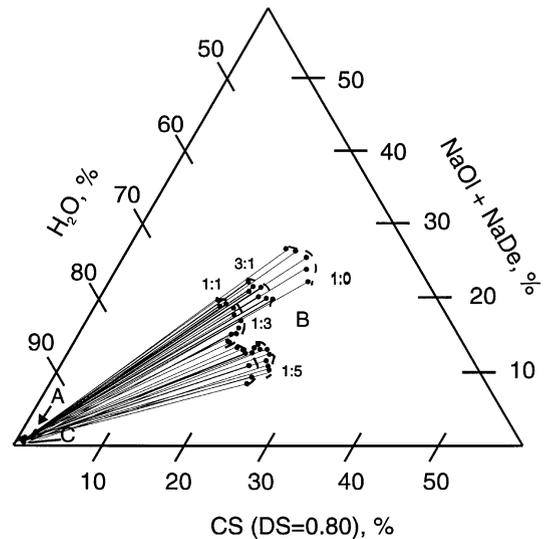


Fig. 6. Partial phase diagram of the system CS (DS=0.80)/NaOl/NaDe/water at 25°C. The NaOl/NaDe ratios were 3:1, 1:0, 1:1 and 1:5. Points marked "A" indicate the compositions prepared in experiments, points marked "B" are the analysed compositions of the gel phase, and points marked "C" represent the compositions of the supernatant aqueous phase.

is obtained by treating the surfactant mixture as one component. The diagram shows only the equilibrium composition of the gels. Typically, the CS/surfactant gels contain 50–70 wt.% water, 10–30 wt.% surfactant and 15–25 wt.% CS. If 50%

of the NaOl is replaced by NaDe, the water content of the gel increases from 55 to 60 wt.%. A further increase of the amount of NaDe does not significantly increase the water content, but the amount of associated surfactant decreases slightly. Apparently, the starch/surfactant interactions are weaker the higher is the fraction of NaDe in the surfactant mixture.

Fig. 7 shows the phase diagram for system containing CS, water and mixtures of NaOl and surfactants with different carbon chain lengths. The water content of the gel phase increases in the order NaOl < NaDod < NaDe < NaOct. Thus, while the CS/surfactant interaction decreases significantly when the chain length decreases, the CS/surfactant ratio in the gels remains quite constant. This shows the importance of charge neutralization as a factor governing complex formation.

3.3.1. Surfactant ratio in the complex phase

Fig. 8 gives the ratio of surfactants in the different CS/surfactant mixture/water phases. The ratio was calculated by analysing the composition of the supernatant phase. The associating mixed

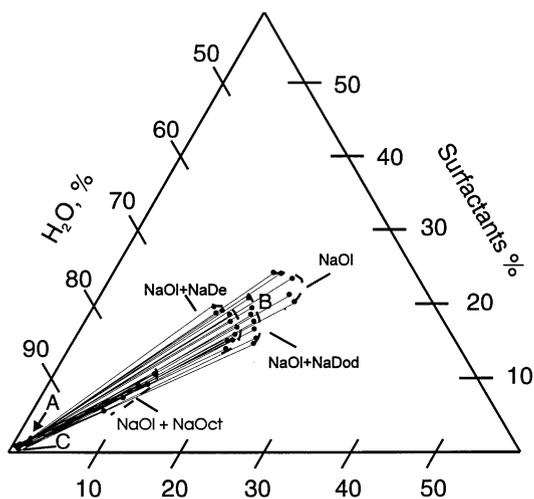


Fig. 7. Partial phase diagram of the system CS (DS=0.80)/NaOl/second surfactant/water at 25°C. The surfactant mixtures were NaOl, NaOl/NaDod, NaOl/NaDe and NaOl/NaOct. The molar ratio of the surfactants in the mixtures was 1:1. Points marked "A" indicate the compositions prepared in the experiment, the points marked "B" are the analysed compositions of the gel phase, and points marked "C" represent the composition of the supernatant aqueous phase.

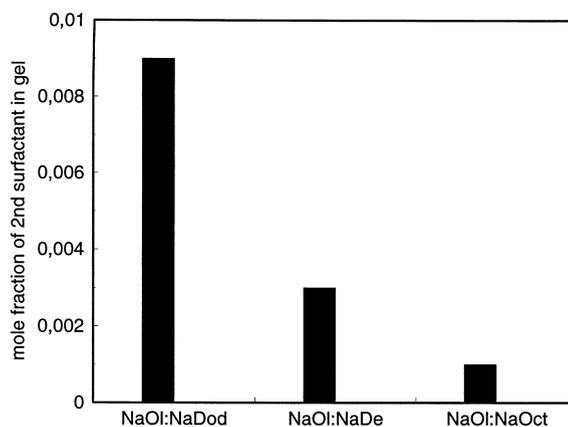


Fig. 8. The mole fraction of the short-chain surfactant in CS (DS=0.80)/surfactant gels in different CS/binary surfactant systems. The mole fraction of the second surfactant was 0.5 of the total surfactant concentration.

micelles contain only a very small fraction of the total amount of short-chain surfactant in the systems. The excess short-chain surfactant mainly functions as a low molecular-weight salt in the solution.

4. Discussion

4.1. Micellisation in surfactant mixtures

4.1.1. Gibbs energy of formation of mixed micelles

In models of mixed micellisation [14], the Gibbs energy of mixed micelle formation is discussed in terms of several contributions.

(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, which depends 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 are crowded into the aggregate surface. This generates steric repulsions between the head groups.

(5) Head group ionic and dipole interactions. For ionic surfactants, repulsive electrostatic interactions arise at the micellar surface. For zwitterionic surfactants, one has to consider the interactions between the permanent dipoles of the polar head groups.

(6) Gibbs energy of mixing of surfactant tails. This contribution accounts for the entropy and the enthalpy of mixing of the surfactant tails of molecules A and B in the hydrophobic core of the micelle.

In the simplest approach, it is assumed that the only contribution to the Gibbs energy of micellisation from the mixing process is the entropy of mixing of the surfactant tails. This ideal mixing model leads to a simple equation for the CMC of n different surfactants:

$$\frac{1}{C_{\text{mix}}} = \sum_{i=1}^n \frac{\alpha_i}{f_i C_i} \quad (1)$$

where C_{mix} is the CMC of the surfactant mixture, α_i is the fraction of surfactant i of the total amount of surfactant, f_i is its activity coefficient and C_i its CMC. In ideal mixed micelles, the activity coefficient f_i is unity. Although few micellar systems behave ideally, this model is useful as a reference system in the description of reasons for non-idealities.

4.1.2. Synergism in mixing of different surfactants

Mixtures of different surfactant types often exhibit synergism in the formation of micelles, i.e. deviations from ideal mixing result in substantially lower CMCs and interfacial tensions than would be expected based on the properties of the unmixed surfactants alone.

The most commonly used models of non-ideal mixing are based on the regular solution approximation. This assumes that the excess Gibbs energy

of mixing consists only of an enthalpy term, while there are no excess entropy contributions. In this model, the micellar mole fractions of a binary surfactant mixture can be calculated by iterative solution of the following expression:

$$\frac{\alpha_1 C_2^* f_2 (1-x_1)}{\alpha_2 C_1^* f_1 x_1} = 1 \quad (2)$$

where C_1^* and C_2^* are the CMCs of the pure component and x_1 is the mole fraction of component 1 in the mixed micelle. The non-ideality is characterised by a net interaction parameter β , which is related to the activity coefficient by:

$$f_1 = \exp[\beta(1-x_1)^2] \quad (3)$$

$$f_2 = \exp[\beta(x_1)^2] \quad (4)$$

From the regular solution theory, it follows that in a binary surfactant system β can be calculated from the CMCs of the surfactant mixtures and the CMCs of the pure components according to:

$$\beta = \frac{\ln[\alpha_1 (C_{\text{mix}}^*/(x_1 C_1^*))]}{(1-x_1)^2} = \frac{\ln\{\alpha_2 C_{\text{mix}}^*/[(1-x_1)C_2^*]\}}{x_1^2} \quad (5)$$

where C_{mix}^* is the CMC of the surfactant mixture.

4.1.3. Mixing two surfactants with same ionic head group

For binary surfactant mixtures with the same end group, a major contribution to the excess Gibbs energy of non-ideal mixing will be due to the volume difference between the hydrophobic tails of the two surfactants. In addition to the effect on the entropy of mixing, which can be accounted for replacing the mole fractions by volume fractions, at any given aggregation number the mean area per molecule in the surface of the mixed micelle will be a non-linear function of the micelle composition. Another source of non-ideality is that ionic interactions at the micelle surface are modified. However, as a first approximation it can be assumed that the polar head group interactions will not be markedly different from those in the single surfactant micelles as long as the ionic strength is kept constant. The conse-

quences of significant variation in the hydrophobic chain length are interesting. Shinoda [15] showed that in potassium tetradecanoate/potassium octanoate mixtures, the less hydrophobic potassium octanoate is almost completely excluded from the micelles.

Our results confirm that micelle formation in mixed sodium alkanolate systems is close to ideal. Fig. 1 shows the CMCs for NaOl/NaDe mixtures predicted by Eq. (1). The system shows only a slightly negative deviation from ideal mixing. Fig. 9 shows the CMCs of the same NaOl/NaDe mixtures, but now the volume differences of the hydrocarbon chains of the two surfactants has been taken into account by using approximate volume fractions instead of mole fractions. The deviation from the theoretical curve taking the free volume differences into account is positive. Thus, while the calculation slightly overestimates the reducing effect of the longer-chain surfactant on the CMC, taking the volume differences into account definitely improves the agreement between the theoretical and experimental values.

Fig. 10 shows the calculated values of the interaction parameter β . The parameter β is negative but quite small over the whole volume fraction range of NaDe. Thus, it can be asserted that the chain-volume differences between NaOl and NaDe are sufficient to explain almost completely the deviations of the surfactant mixture in the micelles from ideal values.

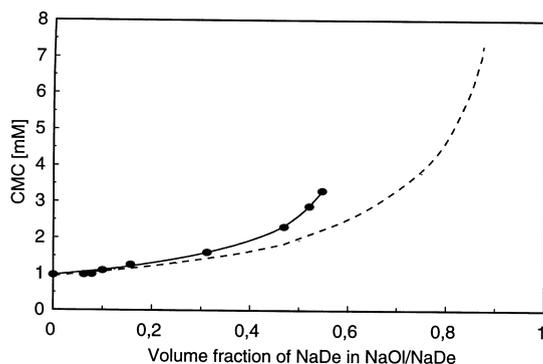


Fig. 9. The CMC of an aqueous NaOl/NaDe solution as a function of the volume fraction of the short-chain surfactant (NaDe). Dashed line: ideal solution, circles: experimental results.

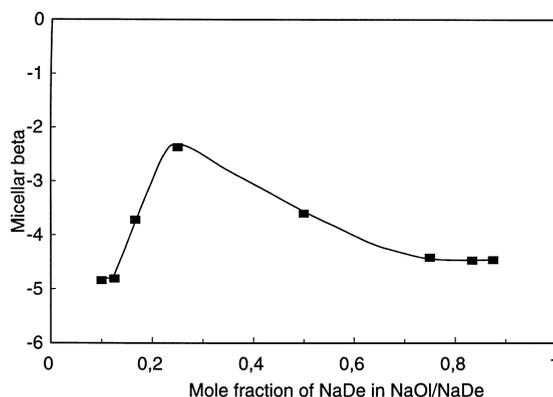


Fig. 10. The non-ideal interaction parameter β_2 in NaOl/NaDe solutions as a function of the volume fraction of NaDe.

4.2. Critical association concentrations

4.2.1. Association with cationic starch

In our previous articles [5,6], we showed that the main interactions controlling CS/surfactant association are the hydrophobic interactions between the hydrocarbon chains of the surfactant and the electrostatic interactions between the cationic starch and the anionic micelles. When another surfactant is added to the system, the packing conditions of the monomers in the micellar aggregates change. Changing the mean size of the hydrophobic tail changes the balance between hydrophobic interactions and electrostatic repulsion.

When the fraction of the less hydrophobic surfactant increases, the CAC also increases. This is analogous to the behaviour of single-surfactant/CS systems, in which the CAC increases when the surfactant chain length decreases. This association is reflected in the dependence of the surface tension and viscosity on the surfactant concentration as a break point in the surface tension and a sudden drop in the reduced viscosity.

In the CS/mixed surfactant systems, the CAC increases markedly when the chain length of the second surfactant decreases in the order NaDod < NaDe < NaOct (Figs. 4 and 5). The mean hydrophobicity of the surfactant mixture is lower the shorter is the chain length of the second surfactant and, by analogy with the formation of

free mixed micelles, micellisation on the polymer chains occurs at higher concentrations (Table 2).

4.2.2. Polymer/surfactant mixture interaction parameter

Polymer/surfactant association can be described as a polymer-induced micellisation. Thus, there is an obvious analogy between mixed micelle formation in pure surfactant systems and the cooperative formation of surfactant aggregates on the polymer in systems of surfactant mixtures and polymers. To illustrate this, we assume that the electrostatic interactions are independent of micellar composition, and that mixed micelle formation on the polycation is completely analogous to the formation of free micelles, except that the presence of the polycation strongly reduces the repulsive electrostatic interactions between the ionic end groups. Then a specific interaction parameter β_{CAC} can be calculated for the mixed micelles associated with the polymer. By analogy with the interaction parameter for free mixed micelles, by substituting the CACs for the CMC in Eq. (5):

$$\beta_{CAC} = \frac{\ln[\alpha_1 CAC_{mix}^*/(x_1 CAC_1^*)]}{(1-x_1)^2} = \frac{\{\alpha_2 CAC_{mix}^*/[(1-x_1)CAC_2^*]\}}{x_1^2} \quad (6)$$

where CAC_1^* is the CAC with surfactant 1, CAC_2^* is the CAC with surfactant 2 and CAC_{mix}^* is the CAC in the surfactant mixture. The values of the specific interaction parameter β_{CAC} can be used as a measure of the synergism in polymer/binary

surfactant systems. Fig. 11 shows β_{CAC} as a function of the mole fraction of NaDe in the system CS/NaOl/NaDe. There is no synergism observed in polymer/surfactant association in the sense that there would be a maximum in the value of β_{CAC} . The interaction parameter is small and changes from negative to positive when the fraction of the short-chain component increases. Thus, mixed micelle formation with the polymer also seems to result in the formation of a remarkably ideal surfactant mixture in the micelles.

4.3. Phase separation and redissolution

Phase separation is a general feature of aqueous systems of a polyelectrolyte and an oppositely charged surfactant. The binding of surfactant results in a complex with a lower charge and hydrophilicity than the initial polymer. When the amounts of the polymer and surfactant are roughly charge-equivalent, the complex precipitates as a water-rich gel. It is well established that phase separation is due to the association of surfactant micelles (in this case, more precisely mixed micelles) with polymer coils. As we have reported previously [5], phase separation takes place at a surfactant concentration somewhat higher than the theoretical charge-neutralization point, but well below the CMC of the pure surfactant. When an excess of surfactant is added, the complex partly redissolves. The redissolution takes place through a charge-reversal mechanism [5].

Figs. 3–5 show that the higher the mole fraction of the short-chain component in the surfactant

Table 2

Critical association concentrations of CS/binary surfactant mixtures (NaOl=sodium oleate, NaDod=sodium dodecanoate, NaDe=sodium decanoate, NaOct=sodium octanoate). The DS of CS was 0.80 and its concentration was 0.01 wt.%

Mole fraction (x_1) of second surfactant	Critical association concentration (mmol dm ⁻³)		
	NaOl/NaDod	NaOl/NaDe	NaOl/NaOct
0	0.05	0.05	0.05
0.25	0.043	0.051	0.053
0.50	0.067	0.075	0.084
0.75	0.089	0.138	0.184
0.83	0.118	0.236	0.295
1	0.120	0.30	0.95

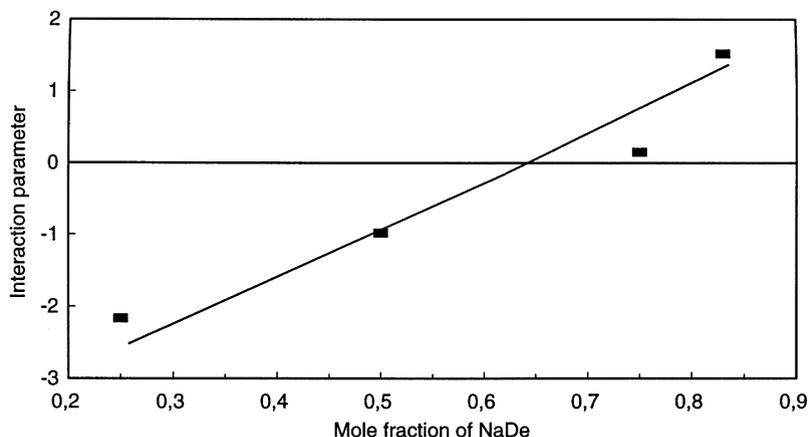


Fig. 11. Calculated polymer/binary surfactant interaction parameter β_{CAC} as a function of the mole fraction of NaDe of the total surfactant concentration in the system CS (DS=0.80, $C=0.01$ wt.%) / NaDe/NaOl.

mixture, the higher is the concentration at which phase separation takes place. This is not surprising, because when the concentration of the short-chain surfactant increases, the fraction of this surfactant in the micelles increases, and hence their hydrophobicity decreases. As expected, redissolution also takes place at higher concentrations when the fraction of the short-chain surfactant increases.

At a given bulk composition, the chain length of the shorter surfactant does not affect the surfactant/polymer ratio in the gel, but the maximum water content of the gel increases strongly when the chain length of the shorter-chain surfactant decreases (Fig. 7). This indicates a reduced hydrophilicity of the complex. Redissolution of the gels takes place at somewhat lower surfactant concentrations when the chain length of the shorter surfactant decreases.

4.4. Surfactant ratio in CS/mixed micelle complex phase

The molar ratio of the surfactants in mixed micelles depends on their chain-length difference. For a given bulk composition, free mixed micelles contain less short-chain surfactant the larger is the difference in chain length. The same behaviour is observed in the CS/surfactant gel (Fig. 8). Thus, the fraction of NaDe in CS/NaOl+NaDe, when the molar ratio of surfactant monomers is 1:1,

is only about 0.003. In systems of CS/NaOl+NaDod, where the chain-length difference of the surfactants is not so large, the corresponding fraction of the NaDod is about 0.009. This again stresses that the association between CS and surfactants can be understood as a polycation-enhanced micellisation of the surfactants on the polymer. A consequence of this behaviour is that the bulk molar ratio of the surfactants does not strongly affect the molar ratio of the surfactants in the aggregate phase. When the bulk fraction of the short-chain surfactant varies from 0.2 to 0.9, its fraction in the gel stays almost constant, at a value of ~ 0.01 . This implies that the long-chain surfactant (NaOl) associates almost totally with cationic starch when the fraction of the short-chain surfactant is sufficiently high. It may even be possible that in this kind of situation, the two surfactants form pure micelles by themselves. Studies of this behaviour will be reported in forthcoming publications.

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