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Determination of the Structure of Complexes Formed by a Cationic Polymer and Mixed Anionic Surfactants by Small-Angle Neutron Scattering

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Aqueous solutions of sodium alkanoates ($C_7H_{15}COONa$, NaOct; $C_9H_{19}COONa$, NaDe; $C_{11}H_{23}COONa$ NaDod; $C_{15}H_{31}COONa$, NaPal) and mixtures of NaPal with NaDod, NaDe, and NaOct, as well as complexes formed by these surfactants with cationic potato starch (CS), were investigated by small-angle neutron scattering (SANS). The results indicate that mixed NaPal/NaDod micelles (without added CS) are prolate ellipsoids with a degree of dissociation of 10–20%. NaPal and NaOct do not form mixed micelles, the effect of NaOct on micelle formation being akin to that of a simple electrolyte. In the NaPal/NaDe systems, which were studied at concentrations between the cmc's of NaPal and NaDe, it can be indirectly inferred from SANS measurements that some NaDe is incorporated in the micelles. NaPal/NaDod systems were investigated at concentrations well above the cmc of the mixture. At such concentrations, the composition of the micelles is equal to the total composition of the surfactant in solution. SANS indicates that the CS molecules have helical conformation. When they associate with surfactants, more compact cylindrical aggregates are formed, in which a core of surfactant is surrounded by the helical chains of CS. In dilute solution, the surfactant monomers do not form micellelike aggregates. The structure of the CS/surfactant complexes is more similar to the inclusion complexes found in amylose–surfactant systems. In mixed systems, the longer chain surfactant is enriched into the surfactant/CS complex.

Introduction

It is well-known from many studies (see, for example, refs 1–4) that in dilute aqueous solutions of polyelectrolyte and oppositely charged surfactant, the surfactant molecules associate with the polymer chains as micellar aggregates or micellelike clusters. In previous papers we have reported on the formation of such aggregates in solutions of cationic starch (CS) and anionic surfactants and surfactant mixtures as well as on the rheological properties of the systems.^{5–7} This system is of particular interest in view of the widespread use of CS as an additive for improving the strength and surface properties of paper. The goal of the investigations described in this report is to clarify how aggregate structure depends on the chain length of the surfactant as well as on micellar composition in solutions containing mixtures of homologous surfactants. The structure of the CS/surfactant aggregates was determined by small-angle neutron scattering (SANS).

The surfactants investigated were sodium alkyl carboxylates.

Scattering techniques are the most important methods used to determine the aggregation number, volume, and average shape of micelles.⁸ SANS has been used in studies of the structure of micelles and intermicellar interactions⁹ and for the determination of micellar charge.¹⁰ SANS has also been applied in the determination of the composition of mixed micelles,¹¹ the location of species in mixed micelles and their relationship to curvature,¹² and the dependence of the charge of micelles on composition of the surfactant mixture¹³ and the temperature.¹⁴ In a SANS study of the interaction of poly(ethylene oxide) with sodium dodecyl sulfate, Cabane et al.¹⁵ found that the sizes of polymer and surfactant aggregates were similar to those in free polymer or surfactant solutions.

It has been known for a long time that amylose forms helical inclusion complexes with a variety of organic compounds, such as lipids,¹⁶ carboxylic acids,¹⁷ and different surfactants.¹⁸ When forming such inclusion complexes,

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amylose assumes to take the so-called V-form conformation. V-amylase is a generic name for crystalline amyloses obtained as single helices when cocrystallized with compounds such as water, iodine, DMSO, alcohols, or fatty acids. In the V-form, a single chain of amylose forms a helix with a relatively large cavity. The central cavities of the ordinary V-forms have a pitch of about 8 Å per turn. A detailed X-ray conformational analysis of the hydrated helix with a guest molecule inside has been reported by Rappenecker et al.¹⁹ Yamamoto et al.¹⁸ found that the binding of sodium alkyl sulfates to amylose is cooperative when the degree of polymerization of polymer is large enough and that the cooperativity depends on the carbon chain length of the surfactant. It has also been suggested that the outer branches of the amylopectin molecule form the same kind of inclusion complexes with suitable lipids.^{20–22} It has been shown that the helical coil formed by the amylose/lipid inclusion complex in aqueous solution involves from six to eight repeating glucose units per helical turn. Antonietti et al.²³ found that complexes are formed by poly-L-lysine with soyllecithin and by κ -carrageenan with cationic dialkyldimethylammonium lipids in which the polymers retain their helical conformation. It has been also reported that anionic sodium carboxyamylose can bind anionic surfactant (SDS).²⁴

Experimental Section

Materials. *Cationic Starch.* Cationic starch (CS), 2-hydroxy-3-trimethylammonium propyl starch, was synthesized from potato starch by Raisio Chemicals Oy, Raisio, Finland. The degree of substitution (DS) was 0.80, as calculated from the nitrogen content. Before cationization the starch was partially depolymerized by oxidation with sodium hypochlorite.

The CS was purified by filtration in a tangential flow ultrafiltration system (Filtron Technology Corporation, Minisette, USA), using a membrane with a cutoff of 8000. The CS was dissolved by heating the CS/water mixture in an autoclave for 30 min at 120 °C. All solutions were prepared at least 24 h before measurements. After this purification the molecular weight distribution of the starch was still quite broad, ranging from 0.1 to 1×10^6 .

Surfactants. All alkanoates (sodium octanoate, C₇H₁₅COONa, NaOct; sodium decanoate, C₉H₁₉COONa, NaDe; sodium dodecanoate, C₁₁H₂₃COONa, NaDod; and sodium palmitate (sodium hexadecanoate), C₁₅H₃₁COONa, NaPal) were synthesized by neutralizing the corresponding acids (purum grade from Fluka A.G.) in alcoholic solution with sodium hydroxide. The salts were purified by recrystallization from acetone.

The deuterated surfactants were synthesized in the same way as the protonated surfactants from deuterated carboxylic acids (C₇D₁₅COOH, 98% D; C₉D₁₉COOH, 98% D; and C₁₅D₃₁COOH, 98% D). The deuterated acids were neutralized with NaOD in C₂H₅OD. All deuterated chemicals were from Medical Isotopes Inc., USA. Critical micelle concentrations of the surfactants and their mixtures are given in Table 1.

Other Chemicals. The water was ion-exchanged and distilled. The deuterium oxide was 99.9% D₂O from Sigma. All other chemicals were analytical grade and were used without further purification.

Neutron Scattering. Small-angle neutron-scattering experiments were carried out with two instruments. The first was the SANS1 instrument at the FRG1 research reactor of GKSS Research Center, Geesthacht, Germany.²⁵ The range of scattering vectors ($0.008 < q < 0.25 \text{ Å}^{-1}$) was covered by three combinations of neutron wavelength (8.5 Å) and sample-to-detector distances (0.7–7 m). The wavelength resolution was 10% (fwhm).

Table 1. Critical Micelle Concentrations of Single Surfactants and Surfactant Mixtures Used in the SANS Measurements

surfactant	surfactant molar ratio	cmc	
		this work (mM)	lit. or theor. (mM)
NaPal		1.62	2.0 (at 50 °C) ^a
NaPal:NaOct	1:1	1.42	3.23 ^b
NaPal:NaDe	1:1	2.78	3.19 ^b
NaPal:NaDod	10:1	1.54	1.77 ^b
	4:1	1.73	1.99 ^b
	2:1	2.04	2.36 ^b
	1:1	2.61	3.06 ^b
	1:2	3.64	4.34 ^b
	1:4	5.32	6.53 ^b
	1:10	8.57	11.1 ^b
NaDod		27.0	26 (at 60 °C) ^a
NaDe		110	106 (at 50 °C) ^a
NaOct		398	385 (at 50 °C) ^a

^a From ref 41. ^b Calculated from measured cmc values using the ideal mixing approximation.

The samples were kept at 70 ± 1 °C in quartz cells with a path length of 1.5 mm. The raw spectra were corrected for backgrounds from the solvent, sample cell, and other sources by conventional procedures.²⁶ The two-dimensional isotropic scattering spectra were azimuthally averaged, converted to an absolute scale, and corrected for detector efficiency by dividing by the incoherent scattering spectrum of pure water,²⁷ which was measured with a 1-mm-path-length quartz cell.

The second SANS instrument was the "MURN" time-of-flight small-angle neutron-scattering spectrometer on the IBR-2 pulsed reactor at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia.²⁸ The scattering vector range was $0.01 < q < 0.4 \text{ Å}^{-1}$, the sample-to-detector distance was 10.5 m, and the neutron wavelength interval was 0.7–5 Å. The intensities, which were recorded by a one-dimensional detector, were corrected for background by subtracting the scattering of the solvent. A vanadium standard was used for calibration.

The data analysis included smearing appropriate to the different instrumental setups. For each instrumental setting, the scattering curves were smeared by the appropriate resolution function. The calculated scattering intensity was fitted to the experimental results by means of least-squares methods.²⁹ The parameters in the models were optimized by conventional least-squares analysis, and the errors of parameters were calculated by conventional methods.³⁰

Model of Mixed Micelles. All scattering intensities of the surfactant mixtures exhibit interference maximum. This indicates that long-range interactions occur between the particles in the studied systems. Because the micelles are charged, it seems reasonable to model the investigated system as a population of particles that interact through diffuse double-layer overlap.

For population of slightly anisotropic or polydisperse particles of number density n , the differential cross sections of neutron scattering per unit volume, $d\Sigma(q)/d\Omega$, can be written as

$$\frac{d\Sigma(q)}{d\Omega} = n\{\langle |P(q)|^2 \rangle S(q) + [\langle |P(q)|^2 \rangle - \langle |P(q)| \rangle^2]\} \quad (1)$$

The scattering vector q is defined by

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$$q = \frac{4\pi \sin \theta}{\lambda} \quad (2)$$

where 2θ is the scattering angle and λ is the wavelength. The form factor $P^2(q)$, which describes the scattering cross section of a single particle, is

$$P^2(q) = \left\{ \int [\rho(r) - \rho_s] \exp(iqr) \, dv \right\}^2 \quad (3)$$

where $\rho(r)$ is the scattering length density of the particle and ρ_s is the scattering length density of the solvent. The structure factor $S(q)$ is given by

$$S(q) = 1 + \frac{1}{V} \int [g(r) - 1] \exp(iqr) \, dv \quad (4)$$

where $g(r)$ is the interparticle correlation function and V is the volume of solution per particle.

In our analysis, we assume that the micelles are monodisperse, prolate, core-and-shell ellipsoids of volume V_2 with the semiaxis a, b, b ($a/b = \gamma$). The volume of the core, which consists of hydrocarbon chains, is V_1 , and its scattering length density is ρ_1 . The volume of the shell, which contains the polar headgroups, is $V_2 - V_1$, and its scattering length density is ρ_2 . Then the single-particle scattering function is given by³¹

$$P(q) = \int_0^1 [V_1(\rho_1 - \rho_s) F(q, R_1) + V_2(\rho_2 - \rho_s) F(q, R_2)] \sin \beta \, d\beta \quad (5)$$

where

$$F(q, R) = 3 \frac{\sin X - X \cos X}{X^3} \quad (6)$$

with

$$X = qR \sqrt{\sin^2 \beta + \gamma^2 \cos^2 \beta} \quad (7)$$

The mean volume of the core, V_1 , can be calculated from molecular group volumes according to

$$V_1 = N_a [\nu(\text{CH}_3) + (\langle n \rangle - 1) \nu(\text{CH}_2)] \quad (8)$$

where N_a is the aggregation number of the micelle. The volume of the shell, V_2 , is given by

$$V_2 - V_1 = N_a \{ \nu(\text{COO}^-) + \varpi_{\text{HG}} \nu(\text{D}_2\text{O}) + (1 - \alpha) [\nu(\text{Na}^+) + \varpi_{\text{Na}} \nu(\text{D}_2\text{O})] \} \quad (9)$$

where

1. $\langle n \rangle$ is the average number of carbon atoms in the hydrocarbon chains of the micelle;

2. $\nu(\text{CH}_2), \nu(\text{CH}_3), \nu(\text{COO}^-)$ are the volumes of, respectively, methylene groups, methyl groups, and headgroups in the surfactant;

3. $\nu(\text{Na}^+)$ and $\nu(\text{D}_2\text{O})$ are the volumes of sodium ions and solvent molecules bound to the surfactant;

4. ϖ_{HG} and ϖ_{Na} are the hydration numbers of the headgroups and of the sodium ion;

5. α is the degree of dissociation of the surfactant molecules in micelle.

The numerical values of the volumes and hydration numbers were taken from ref 32.

The second term of eq 1 can be calculated using the decoupling approximation;³³ i.e., it is assumed that there is no correlation between interparticle separation and particle size, and no

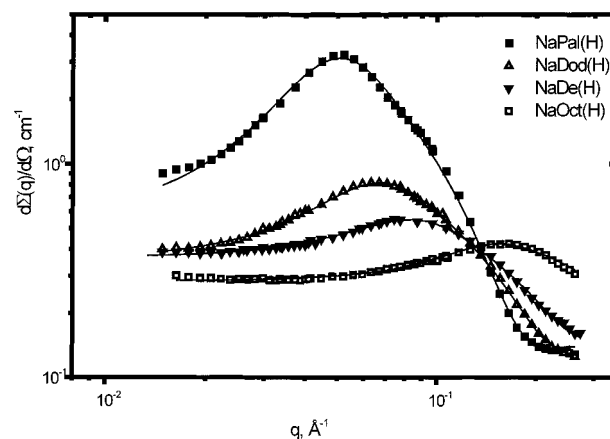


Figure 1. Differential cross section of SANS from solutions of single surfactants (nondeuterated) in heavy water as well as the curves fitted using eq 6. Surfactant concentrations: NaPal and NaDod, 100 mM; NaDe, 200 mM; NaOct, 600 mM.

correlation between interparticle distances and particle orientation. This assumption is reasonable for dilute solutions of charged micelles if γ is not much greater than 1. In our analysis, we used the rescaled mean spherical approximation (RMSA) structure factor for dilute dispersions of charged colloidal particles calculated by Hansen and Hayter¹⁰

$$S(q) = \frac{1}{1 - 24\eta G(q, R_{\text{HS}}, \eta_{\text{HS}}, Z_{\text{eff}})} \quad (10)$$

where η is the volume fraction of particles. The exact expression for $G(q, R_{\text{HS}}, \eta_{\text{HS}}, Z_{\text{eff}})$, which is a function of effective hard sphere radius R_{HS} , the hard sphere volume fraction η_{HS} , and the effective charge Z_{eff} , has been derived by Hayter and Penfold³⁴ and Hansen and Hayter.¹⁰

It is assumed that the interparticle interactions are due to interactions between the diffuse double layers surrounding the micelles. The interaction potential between two similar spherical micelles of mean diameter $\langle d \rangle$ at distance r between their centers is given by

$$V(r) = 2\pi\epsilon_0\psi_0^2 \langle d \rangle \exp[-\kappa(r - \langle d \rangle/2)] \quad (11)$$

where ψ_0 is the surface potential, ϵ_0 is the permeability of a vacuum, and ϵ is the dielectric constant of the solution between the micelles. κ is the Debye–Hückel inverse screening length, determined by the ionic strength of the solution. To a good approximation, the surface potential is related to the charge z on the micelle, by³⁵

$$\psi_0 = \frac{z}{\langle d \rangle \pi \epsilon_0 (2 + \kappa \langle d \rangle)} \quad (12)$$

For the fitting procedure, we used a FORTRAN program written by J. B. Hayter.³⁴ The fitting parameters were aggregation number, degree of dissociation α , axial ratio γ , residual background, and the correction of the normalization parameter (interval 0.8–1.2).

The number of fitting parameters is sufficiently small compared to the information content of the scattering patterns so that least-squares methods can be applied with statistical significance.³⁶

Results and Discussions

Single-Surfactant Micelles. Figure 1 shows the differential cross section of SANS from solutions of single surfactants in heavy water as well as the curves fitted

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Table 2. Parameters Obtained by Fitting Eq 6 to Experimental Data for Solutions of Single Surfactants in Heavy Water

surfactant	concn. (mM)	N_a	average diameter (Å)	axial ratio	average no. charges, e_0	degree of dissoc., α
sodium palmitate, NaPal	100	161 ± 6	71 ± 2	2 ± 0.2	19 ± 2	0.12
sodium dodecanoate, NaDod	100	75 ± 3	52 ± 2	1.5 ± 0.1	11 ± 1	0.21
sodium decanoate, NaDe	200	53 ± 2	45 ± 2	1.5 ± 0.1	16 ± 2	0.35
sodium octanoate, NaOct	600	38 ± 3	32 ± 5	1 ± 0.1	4 ± 2	0.13

using eq 6. Note that the concentration is different for the different surfactants. The intensity increases and the position of the interference maximum shifts to lower q values when the alkyl chain length increases. This shows that larger micelles are formed by surfactants with longer alkyl chain, as is well-known from earlier studies.⁸ Agreement between theoretical curves and experimental data is excellent; i.e., the model of micelles as prolate rotational ellipsoids interacting through a screened Coulomb potential satisfactorily describes the experimental data. The small deviation at the lowest q range is probably due to the limitations of instrumental resolution.

Parameters obtained by the fitting procedure are given in Table 2. When the chain of the surfactant becomes shorter, the average diameter of the micelles decreases from 71 ± 2 Å (NaPal) to 31 ± 5 Å (NaOct) with simultaneous change in the micellar shape from prolate ellipsoid with axis ratio 2.0 ± 0.2 (NaPal) to spherical (NaDe and NaOct). The degree of dissociation increases in the order NaPal < NaDod < NaDe, which agrees with many other observations of the dependence of α on chain length. The lower value of α for NaOct is probably due to experimental inaccuracy.

Mixed Micelles. Solutions of NaPal(H)/NaDod(H), NaPal(H)/NaDe(H), and NaPal(H)/NaOct(H) in heavy water were investigated (molar ratio 1:1, (H) indicates hydrogen-based surfactants). The results were compared to measurements on similar solutions of NaPal(D)/NaDod(H), NaPal(D)/NaDe(H), and NaPal(D)/NaOct(H), where (D) denotes deuteration. The total surfactant concentration was 100 mM, which is above the cmc of pure NaPal and NaDod but below the cmc of NaDe and NaOct. The results are shown in Figure 2a,b. Marked formation of mixed micelles is detected only in the NaPal/NaDod system. Owing to the large difference in the scattering length densities, the ratio of the scattering intensity from NaPal(H) in D₂O to the scattering from NaPal(D) in D₂O is ~ 100 . It is not possible to detect pure NaPal(D) micelles in D₂O by SANS. q at the interference maximum is equal for NaPal(H)/NaDod(H) and NaPal(D)/NaDod(H), which indicates that the concentration of micelles is the same in both solutions. From the intensity ratio of NaPal(D)/NaDod(H) to NaPal(H)/NaDod(H) it can be estimated³⁷ that the fraction of NaPal molecules in the mixed micelle is 0.49 ± 0.02 . Thus, the composition of the mixed micelles is the same as the total composition of surfactant in solution. This result confirms that at concentrations much higher than the cmc of a surfactant mixture, the composition of the micelles is approximately the same as the total composition of the surfactants in solution.³⁸

There is no sign of scattering from micelles in the curves for NaPal(D)/NaOct(H) and NaPal(D)/NaDe(H) (Figure 2b). This indicates that in 100 mM NaPal/NaDe and 100 mM NaPal/NaOct only pure NaPal micelles are formed. However, the size and interactions of the micelles are affected in different ways by NaDe and NaOct.

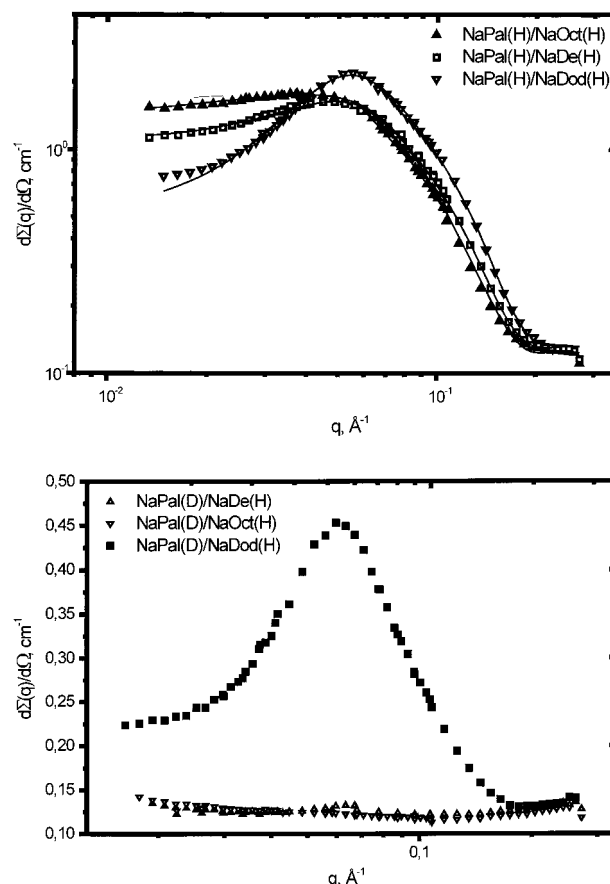


Figure 2. (a, top) Differential cross section of SANS from solutions of 1:1 surfactant mixtures (nondeuterated) in heavy water as well as the curves fitted using eq 10. Total surfactant concentrations: 100 mM. (b, bottom) Differential scattering cross section for SANS from solutions of 1:1 mixtures of deuterated NaPal and nondeuterated surfactants with shorter chains in heavy water, as well as the curves fitted using eq 10. Total surfactant concentrations: 100 mM.

Addition of NaDe increases the effective micellar charge. This effect leads to significant intermicellar interactions, as shown by the maximum in the scattering intensity. Thus, it seems that NaDe is to some extent incorporated in the micelles. Presumably, because the total concentration is below the cmc of pure NaDe, very small amounts of the surfactant are incorporated so that the micelles cannot be detected by SANS when the NaPal contrast is low.

In the model calculations (drawn lines in Figure 2), it was assumed that the micelles in NaPal(H)/NaDe(H) and NaPal(H)/NaOct(H) contain only NaPal and that the NaPal/NaDod ratio in the micelles is 1:1, i.e., the same as in bulk solution. The agreement between the theoretical curves and experimental data is as good as for single-surfactant solutions. The dimensions of the mixed NaPal(H)/NaDod(H) micelles in 1:1 solutions lie between those of pure NaPal and pure NaDod (Table 3). The surface charge is closer to the charge of pure NaDod micelles.

When the same fitting procedure was applied to the data for NaPal(D)/NaDod(H), N_a turned out to be about

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Table 3. Parameters Obtained by Fitting Eq 6 to Experimental Data for Solutions of Mixed Surfactants in Heavy Water

surfactant	concn. (mM)	N_a	average diameter (Å)	axial ratio	average no. charges (e_0)	degree of dissociation, α
NaPal(H)/NaDod(H)	100	137 ± 4	66 ± 2	1.7 ± 0.1	10 ± 1	0.07
NaPal(D)/NaDod(H)	100	124 ± 3	64 ± 2	1.0 ± 0.1	11 ± 7	0.09
NaPal(H)/NaDe(H)	100	132 ± 4	65 ± 2	1.8 ± 0.2	29 ± 4	0.22
NaPal(H)/NaOct(H)	100	179 ± 5	73 ± 2	1.7 ± 0.1	18 ± 2	0.10

10% smaller than for NaPal(H)/NaDod(H). The degree of dissociation is about the same, and the axial ratio is only 1.0. A possible explanation is that the NaPal and NaDod molecules are not evenly distributed in the prolate micelles. The radius of the cylindrical part of the prolate micelle is clearly closer to the chain length of the NaDod than to that of NaPal. This implies that the middle part of the micelle must be enriched in NaDod, with NaPal located close to the end caps. Accordingly, SANS detects an aggregate with lower axial ratio in the NaPal(D)/NaDod(H) system, where only NaDod contributes to the scattering. It is not quite clear why this situation should be energetically favorable, as the mean radius of curvature is smaller in the end caps, and the bending energy of a mixed surfactant bilayer should be lower the higher the fraction of short-chain surfactant.^{39,40}

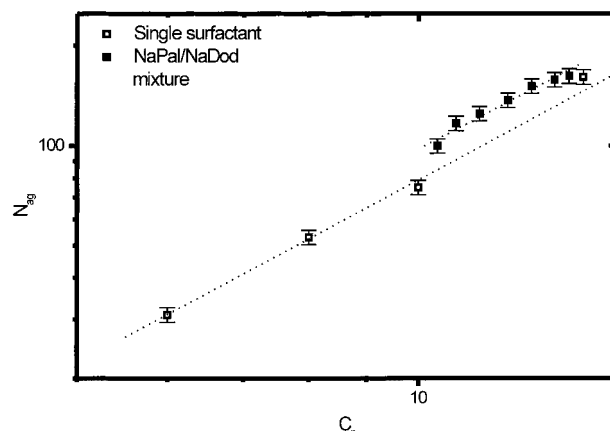
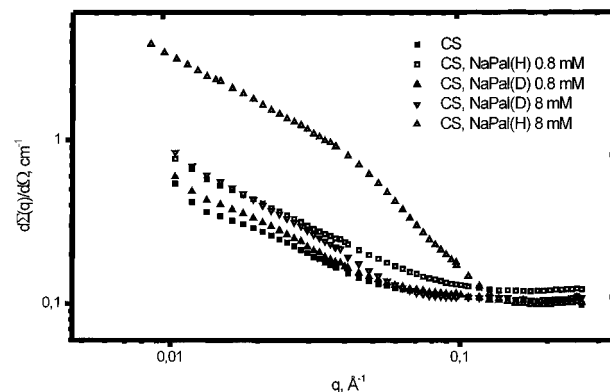
The results from fitting the theoretical curves to the results from NaPal(H)/NaDe(H) and NaPal(H)/NaOct(H) solutions confirm that the effects of NaDe and NaOct on NaPal micelles are different.

The micelles in the NaPal/NaOct solution are larger than the micelles in NaPal/NaDe or NaPal solutions (Tables 2, 3). As expected, the micelles consist almost entirely of NaPal because the concentration of NaOct is far below its cmc, so that it should have little tendency to participate in micelle formation. Thus, the effect of NaOct is mainly that of a simple electrolyte that promotes micelle formation by screening of electrostatic repulsion. The result is that the micelles formed by NaPal grow slightly, intermicellar interactions decrease, and the interference maximum almost disappears.

The micellar aggregation number in 100 mM NaPal/NaDe is lower than in 100 mM pure NaPal, while the degree of dissociation increases. The smaller size could be due to the lower concentration of NaPal in the mixed system, but the higher charge and the fact that NaDe does not affect micellar properties in the same way as NaOct indicate that NaDe does participate in some way in micelle formation, although this cannot be directly detected by SANS. NaDe (50 mM) is much closer to its cmc than NaOct (50 mM), so that this conclusion does not seem unreasonable.

Figure 3 shows the dependence of the aggregation number of mixed NaPal/NaDod micelles on the mean chain length of the surfactant at constant surfactant concentration (100 mM).

In the evaluation of aggregation numbers, we assumed that the composition of the micelles is the same as the bulk composition of surfactant. The sizes of both the mixed micelles and the single surfactants grow at about the same rate when the alkyl chain length increases. However, the values of N_a of the mixed micelles are slightly larger than those inferred from the values of single surfactants by linear interpolation. Indeed, some synergism in the

**Figure 3.** Mean aggregation number of mixed NaPal/NaDod micelles as a function of the mean chain length of the surfactant. The carbon number means the number of the CH₂– groups of the alkyl chain. Also shown are the aggregation numbers of pure single-chain surfactants.**Figure 4.** Differential scattering cross sections for SANS from 0.8% cationic starch and different concentrations of NaPal in heavy water.

formation of mixed micelles formed by surfactants with different alkyl chain is to be expected,⁴⁰ as also shown by the values of the cmc's for mixtures (Table 1).

CS/Surfactant Complexes. The cationized and depolymerized starch used in these studies has a M_w of about 6×10^5 , which implies that it consists of molecules of quite the same size as native potato amylose. It carries high charge owing to the quaternary ammonium substituents. This strengthens the interaction between CS and oppositely charged surfactants significantly and thus should promote association. The conventional theory of polymer–surfactant association assumes that the surfactant monomers are associating to the polymer chain as micelles or micellelike aggregates. As we will show below, the helical conformation of the cationic starch seems to result in a different type of structure, i.e., the formation of inclusion complexes.

Figure 4 shows SANS from a 0.8% solution of CS in D₂O to which has been added different concentrations of surfactant (NaPal). The compositions were chosen so that the scattering from CS could be separated from the scattering of CS/surfactant aggregates. Thus, CS/surfac-

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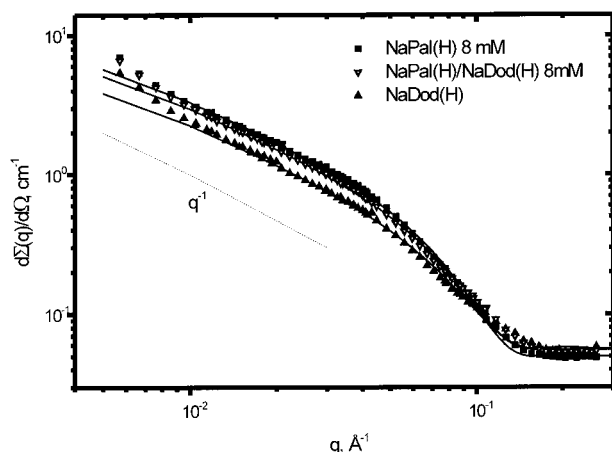


Figure 5. Differential scattering cross sections for SANS mixtures of cationic starch (CS) and protonated surfactants in D₂O. The concentration of CS is 0.8%. The surfactants and their concentrations are given in the figure. NaPal(H) and NaDod(H) are mixed in the molar ratio 1:1. Solid lines are fits by the cylindrical model in eq 13.

tant aggregates should be seen with the combination CS/NaPal(H)/D₂O, while only CS should be seen with the combination CS/NaPal(D)/D₂O. NaPal was chosen because it forms the largest micelles of the investigated surfactants.

The differential scattering intensities immediately indicate that two processes take place in the system as the surfactant concentration increases: on one hand, the formation and growth of CS/surfactant complexes and, on the other hand, changes in the conformation of CS. The scattering at low values of q suggests that the overall size of the aggregates is larger than the experimental interval of scattering vectors so that the scattering cross sections observed are essentially due to intraparticle interactions. For this reason, and because the CS neutralizes the charge of the surfactant aggregates, interparticle interactions were neglected in the analysis of scattering data.

Figure 5 shows differential SANS cross sections for CS/NaPal(H), CS/NaPal(H)/NaDod(H), and CS/NaDod(H) mixtures. The concentration of CS and the total surfactant concentration is the same in all systems (0.8% and 8 mM, respectively). The surfactant concentration is much higher than the critical association concentration of CS/NaPal ($c_{ac} \sim 0.01$ mM) so that significant amounts of CS/surfactant complexes should be present. The scattering intensities indicate that the largest complexes occur in the CS/NaPal system and that the difference between CS/NaPal and CS/NaPal/NaDod complexes is smaller than the difference between CS/NaPal/NaDod and CS/NaDod complexes. Apparently, NaPal is enriched in the complex phase formed by the NaPal/NaDod mixtures.

When interparticle interactions are neglected, the differential scattering cross section can be written

$$\frac{d\Sigma(q)}{d\Omega} = \frac{d\Sigma(0)}{d\Omega} P^2(q) + B \quad (13)$$

where $d\Sigma(0)/d\Omega$ is the scattering at “zero” angle and B is the incoherent scattering background. $d\Sigma(0)/d\Omega$ is related to concentration of particles (N_v), volume (V), and scattering length densities by

$$\frac{d\Sigma(0)}{d\Omega} = N_v (\langle \rho \rangle - \rho_s)^2 V^2 \quad (14)$$

where $\langle \rho \rangle$ is the average scattering length density of the

particle. The slope of a log/log plot of the differential cross section vs q is close to -1 , which indicates that elongated structures are formed. Therefore, in our analysis of experimental data, we assume that the aggregates are cylindrical. In this case single particle scattering function $P^2(q)$ is equal to $\langle F^2(q) \rangle$, where $F(q)$ is a form factor of a cylinder written as

$$F(q) = \int_0^{\pi/2} \frac{\sin(qL/2 \cos \beta) 2J_1(qR \sin \beta)}{(qL/2 \cos \beta)(qR \sin \beta)} \sin \beta d\beta \quad (15)$$

where L is the length and R is the radius of the cylinder, J_1 is the first-order Bessel function, and β is the angle between the q vector and the axis of the cylinder.

Four parameters were varied in the fitting of theoretical differential cross sections to experimental results: R , L , $d\Sigma(0)/d\Omega$, and B_{inc} . The model describes the experimental data for q values larger than 0.01 Å^{-1} . The deviations at lower q could be due to the presence of some much larger particles (possibly some incompletely dissolved CS). Parameters obtained by the fitting procedure are given in Table 4.

The first row in Table 4 shows that that pure CS in solution exhibits local cylindrical behavior (radius of cylinder 30 Å). Probably the pure CS solution contains cylinder-like aggregates in the size range investigated. The cylinder length is $\sim 600 \text{ Å}$. In the q interval used it is difficult to estimate this parameter more accurately, but this is a very reasonable value for starch with the molecular weight of the CS, assuming that it has a helical conformation.

The radius of the cylindrical CS/surfactant aggregates decreases when the surfactant concentration increases. This result is expected because when surfactant associates with the CS the repulsion between the cationic substituent groups decreases so that the conformation of the CS molecules would become more compact. Hydrophobic interactions between the surfactant chains may also contribute.

When deuterated surfactants are used (Figure 6), the intensities are only about a tenth of the intensities recorded for protonated surfactants. This confirms that the fraction of surfactants in the CS/surfactant complexes is high. They fall in the same range as for cationic starch without surfactant (Figures 2 and 4). However, the dependence of the scattering cross section on q^{-1} still indicates the formation of cylindrical aggregates. The scattering of mixed NaDod(D)/NaPal(D)/CS aggregates is lower than that for pure NaDod(D)/CS or NaPal(D)/CS. The reason for this is not clear; it may be an experimental artifact.

In the analysis of surfactant systems, the length of the cylinder was kept constant and only its radius was adjusted. The cylinder radius of deuterated complexes is larger than the radius obtained for fully protonated complexes. This suggests that the surfactant molecules are inside the CS/surfactant complexes with the CS molecules forming some kind of shell around the surfactant aggregates. Owing to the low intensity of scattering from CS, the contribution of CS shell scattering is less visible in CS/NaPal(H), CS/NaDod(H), and CS/NaPal(H)/NaDod(H) mixtures. The application of a homogeneous model (homogeneous cylinder) gives different “effective radii”—smaller for mixtures containing protonated surfactants and larger for mixtures with deuterated surfactants.

An explanation for the large difference in intensities between scattering from pure CS and CS containing

Table 4. Dimensions of Cationic Starch (CS)/Surfactant Complexes^a

surfactant	concn. (mM)	radius (Å)	length (Å)	$d\Sigma(0)/d\Omega$ (cm ⁻¹)	V_f
NaOct(H)	8	30.3 ± 0.5	630	3.1 ± 0.2	
NaDe(H)	8	31.3 ± 0.1	630	5.2 ± 0.3	
NaDod(H)	0.08	25.2 ± 0.2	630	8.9 ± 0.3	
NaDod(H)	0.08	29.8 ± 0.2	630	3.4 ± 0.1	
NaDod(H)	0.8	29.0 ± 0.2	630	4.3 ± 0.1	
NaDod(D)	0.8	33.0 ± 0.2	630	3.56 ± 0.05	0.08 ± 0.01
NaDod(H)	8	23.8 ± 0.1	630	19.7 ± 0.6	
NaDod(D)	8	37.8 ± 0.2	630	4.9 ± 0.1	0.45 ± 0.04
NaPal(H)	0.8	26.1 ± 0.2	630	5.5 ± 0.2	
NaPal(D)	0.8	30.3 ± 0.5	630	3.60 ± 0.05	0.17 ± 0.02
NaPal(H)	8	24.9 ± 0.1	630	29.5 ± 0.6	
NaPal(D)	8	38.0 ± 0.2	630	5.9 ± 0.1	0.49 ± 0.4
NaPal(H)/NaDe(H)	8	23.7 ± 0.1	630	23.3 ± 0.6	
NaPal(D)/NaDe(H)	8	32.1 ± 0.1	630	7.1 ± 0.1	0.41 ± 0.4
NaPal(H)/NaDod(H)	8	24.5 ± 0.1	630	26.1 ± 0.6	
NaPal(H)/NaDod(D)	8	29.0 ± 0.1	630	18.2 ± 0.4	0.15 ± 0.2
NaPal(D)/NaDod(H)	8	29.4 ± 0.1	630	11.7 ± 0.3	0.29 ± 0.2
NaPal(D)/NaDod(D)	8	33.2 ± 0.2	630	4.0 ± 0.1	0.55 ± 0.05

^a The concentration of CS was 0.8% (by weight) in all solutions. V_f = volume fraction of deuterated surfactant in the aggregates.

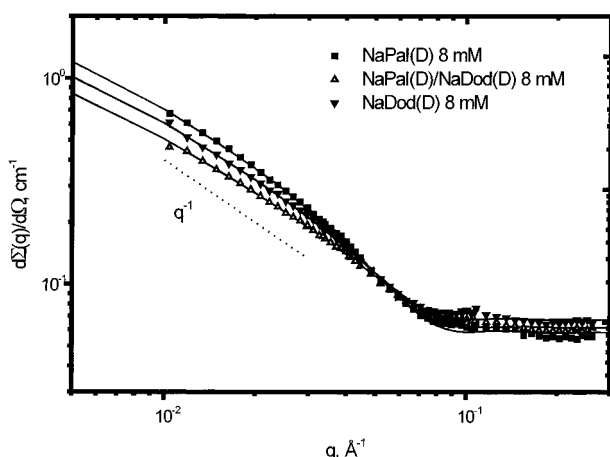


Figure 6. Differential scattering cross sections for SANS mixtures of cationic starch (CS) and deuterated surfactants in D₂O. The concentration of CS is 0.8%. The surfactants and their concentrations are given in the figure. NaPal(D) and NaDod(D) are mixed in the molar ratio 1:1. Solid lines are fits by the cylindrical model in eq 13.

protonated surfactants is that the hydrogen atoms (H) in CS are extensively substituted by D from solvent.

The scattering at “zero” angle ($d\Sigma(0)/d\Omega$) obtained from the fitting of parameters can be used to determine the volume fraction of surfactant in CS/surfactant complexes. This is possible because we also investigated mixtures of protonated and deuterated surfactants. The volume fraction (V_f) of substituted surfactant is given by

$$V_f = \frac{(\sqrt{R_s} - 1)(\rho_{\text{surfactant(H)}} - \rho_s)}{(\rho_{\text{CS}} - \rho_{\text{surfactant(H)}}) - \sqrt{R_s}(\rho_{\text{surfactant(D)}} - \rho_{\text{CS}})} \quad (16)$$

where

$$R_s = \frac{d\Sigma(0)}{d\Omega_{\text{CS/surfactant(H)}}} / \frac{d\Sigma(0)}{d\Omega_{\text{CS/surfactant(D)}}} \quad (17)$$

and ρ denotes scattering length densities of CS, solvent (D₂O), and protonated and deuterated surfactant. The volume fraction of surfactant is shown in Table 4. As expected, it increases with increasing surfactant concentration. The high volume fraction in 8 mM solution

Table 5. The Dimensions of CS/Surfactant Aggregates Determined by Using the Shell–Core Model^a

surfactant	NaPal	NaPal/NaDod	NaDod
R_{out} (Å)	35.5 ± 0.5	33.5 ± 0.5	34.0 ± 0.5
R_{in} (Å)	3.3 ± 0.1	3.1 ± 0.1	2.5 ± 0.1
L (Å)	630	630	630
aggregation number of surfactants, NA	39 ± 1	39 ± 1	33 ± 1

^a The concentration of cationic starch was 0.8 wt%, and the total surfactant concentration was 8.0×10^{-3} mol/dm³.

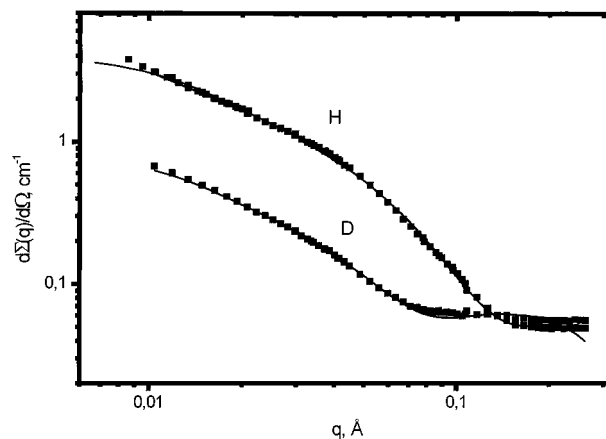


Figure 7. Differential scattering cross sections for SANS mixtures of cationic starch (CS) with protonated (H) and deuterated (D) NaPal in D₂O modeled by using the core–shell model. The CS concentration was 0.8 wt %, and the NaPal concentration was 8 mM.

supports the assumption that aggregates at this concentration have a low charge so that interparticle interactions (structure factors) can be neglected.

The single-particle scattering function of a two-shell cylinder $P^2(q)$ can be expressed in the same way as for a two-shell prolate ellipsoid (eq 5, Figure 7), using the form factor of a cylinder (eq 15). The calculated dimensions of aggregates of CS and NaPal are length of aggregate ~ 630 Å, radius of the outer cylinder (formed by CS) ~ 35.5 Å, and radius of the inner cylinder (formed by NaPal) ~ 3.3 Å. While the values of the dimensions and aggregation numbers are relatively uncertain, there is no doubt that the results indicate that NaPal, in contrast to many other complexes of oppositely charged polymer–surfactant complexes, does not form spherical or ellipsoidal micellar aggregates when associating with CS. Table 5 shows some

properties of other CS/surfactant complexes analyzed by using this shell–core model. When the chain length of the surfactant decreases (from C₁₆ to C₁₂), the radius of the shell as well as the radius of the core decreases. This is a very obvious result because the volume of hydrocarbon chains of the surfactants decreases. The values of structure parameters of complexes of mixed CS/NaPal/NaDod aggregates are between the values of parameters of CS/NaPal and CS/NaDod aggregates.

In conclusion, the core–shell model (identical geometrical parameters) satisfactory describes SANS data simultaneously for CS/surfactant(H) and CS/surfactant-(D). Thus, the structure of the complexes can be roughly

described as a core/shell cylinder. The shell is formed by the CS chains, which in the same way as the amylose and also partly amylopectine have helical conformation. The core consists of surfactant chains. Thus, the structure of the CS/surfactant complexes is similar to that of inclusion complexes of amylose and surfactants, but apparently the cooperativity is much stronger owing the electrostatic attraction between the headgroups of the surfactant and the cationic groups in CS, so that aggregates are formed at very low concentrations with a relatively well-defined critical association concentration.

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