FORMATION OF ORGANIZED STRUCTURES IN SYSTEMS CONTAINING ALKYLPYRIDINIUM SURFACTANTS AND SODIUM POLY(STYRENESULFONATE)[#]

Ksenija Kogej,*[a] Elisabeth Theunissen,[b] and Harry Reynaers[b]
[a]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-1000 Ljubljana, Slovenia*
[b]*Department of Chemistry, Catholic University of Leuven, Celestijnenlaan 200F,*
B-3001 Heverlee, Belgium

[#]Dedicated to Professor Davorin Dolar on the occasion of his 80th birthday.

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Abstract

Synchrotron X-ray scattering was used for structural investigations in systems of sodium poly(styrenesulfonate) (NaPSS) and dodecyl- (DPC) and cetylpyridinium chlorides (CPC) at various surfactant to polyelectrolyte (S/P) molar ratios. From the Bragg peaks emerging in the scattering curves two types of organization of surfactant in conjunction with the polyion are proposed. In NaPSS/DPC (all S/P values) and in NaPSS/CPC complexes ($S/P \leq 0.7$) the surfactant is aggregated into spherical polyelectrolyte-induced micelles. These micelles are smaller in size than the ordinary ones. By increasing the S/P ratio, they grow in size, whereas the number of micelle-like aggregates per polyion-chain remains approximately constant. In the NaPSS/CPC precipitate ($S/P \geq 1$) a hexagonal phase is observed with a unit cell constant equal to 39.5 Å in which micelles change into a cylindrical shape. No similar crystalline-like structure was observed in complexes with DPC.

Introduction

Ionic surfactants form complexes with oppositely charged polyelectrolytes already in extremely dilute solutions.[1-3] In general, the complexation reaction results in phase separation whereby an insoluble complex between the polyelectrolyte and the surfactant is formed. In conjunction with the polyelectrolyte, the surfactant is aggregated into the so-called polyion induced micelles, in which the added polyion has the effect of connecting the oppositely charged surfactant aggregates together. Various ordered structures have been observed in such precipitates or highly dense phases. Carnali[4] found a hexagonal phase in the phase diagram of 50 % neutralized sodium poly(acrylate), (NaPA) tetradecyltrimethylammonium bromide, and water. Likewise, Ilekti et al.[5] found cubic, hexagonal and lamellar phases in a phase diagram of stoichiometric complexes between NaPA and cetyltrimethylammonium bromide. In the work reported here, our purpose is to obtain information about the structural properties of complexes formed between sodium poly(styrenesulfonate) (NaPSS) and dodecyl- (DPC) and cetylpyridinium chlorides (CPC). The binding of cetylpyridinium cation (CP^+) by poly(styrenesulfonate) anion (PSS^-) is one of the strongest ones observed. It starts at free surfactant concentration in water around 10^{-8} mol/L and continues to almost quantitative association (100% binding).[2,3] The binding of dodecylpyridinium cation (DP^+) is less strong; it is shifted to free DPC concentration around 10^{-6} mol/L and reaches around 80%.[2,3] We presume that these strong interactions are reflected also in the structural properties of complexes. The latter will be examined by means of synchrotron X-ray scattering (SAXS) in a wide range of surfactant to polyelectrolyte molar ratios.

Experimental section

Materials and Preparation of Samples

Sodium poly(styrenesulfonate) (NaPSS) with a molar mass of about 70 kg/mol and a degree of sulfonation of 1.0, supplied by Polysciences, Inc. (Warrington, PA) was prepared and purified by the procedure described in literature.[2] The surfactants, N-cetylpyridinium chloride (CPC, puriss, Kemika Zagreb, Croatia) and N-dodecylpyridinium chloride (DPC, a gift from Merck-Schuchardt), were repeatedly recrystallized from acetone and dried under vacuum at 50 °C. All solutions were prepared with ultra pure water obtained from the Milli-Q-Reagent Grade Water System, Millipore.

The mixed NaPSS/DPC and NaPSS/CPC solutions were prepared by slowly adding an appropriate amount of DPC or CPC stock solution in water to a stock solution of NaPSS at room temperature under stirring.[6-7] The total polyelectrolyte concentration in the final mixed solutions was 0.05 moles of monomer units per volume of solution. The solutions were studied in a wide range of surfactant to polyelectrolyte molar ratio, denoted by S/P, from 0 up to 1.5 (S/P was calculated as the ratio between the number of moles of surfactant and of the monomer units of the polyelectrolyte, respectively). The samples are completely transparent up to S/P ratios a little above 0.7.[6-9] At higher surfactant content, the solutions become turbid and at approximately 1:1 molar ratio a white complex phase-separates from the solution. The PSS^-/DP^+ complex is a slightly sticky phase, whereas the PSS^-/CP^+ one is a powderlike white precipitate. The equilibrium solution is a transparent waterlike phase. It contains a rather low amount of excess surfactant and NaCl. The latter one results from the complexation reaction between the polyelectrolyte and surfactant.[6,7,10]

Synchrotron X-ray measurements. Small-angle X-ray experiments were performed on the SAXS/WAXS beam line BM26 (DUBBLE) at the European Synchrotron Radiation Facility (ESRF, Grenoble).[11] The samples for SAXS measurements were filled in a thermally isolated sample holder, which was kept at 25°C. The details in connection with the experiments are described elsewhere.[6,7] The range of the scattering vector $|\mathbf{q}|$ ($q = (4\pi/\lambda)\sin\theta$, where θ is the wavelength of the incident beam and 2θ is the scattering angle) studied was from 0.01 to 0.5 Å^{-1}. Silver behenate was used as a low-angle diffraction standard to check the proper alignment and to calibrate the instrumentation. The SAXS data were normalized to the intensity of the primary beam and corrected for the detector response. The background scattering due to the solvent was subtracted from the scattering curves by taking into account the differences in the absorption of the solution and the solvent. For the preliminary treatment of data the software packages BSL[12] and FIT2D[13] were used.

General Remarks on Scattering Curves from Surfactant-Polyelectrolyte Solution. The appearance of diffraction peaks in the SAXS profiles is an indication of a high degree of order in the system. Scherrer[14] showed that the mean crystallite size in a given sample is related to the pure X-ray diffraction line broadening and may be estimated from Bragg peaks by the equation:

$$L = \frac{\lambda}{\beta_S \cos\theta} \tag{1}$$

where β_S is the full width at a half-maximum intensity of the peak. The value of β_S is obtained by modeling the Bragg peak in SAXS curves using a Gaussian function. Parameter L is a measure of the mean long-range order in the system. Moreover, an "interaction radius" (r_m) of the scattering entities and a degree of disorder ($\Delta/\bar{a}$) in the system can be obtained from expressions (2) and (3)[15]

$$r_m = \left(\frac{\pi}{2.5}\right)^2 \frac{\lambda}{\beta_S} \tag{2}$$

$$\Delta/\bar{a} = \frac{1}{\pi}\sqrt{\frac{\beta_S \bar{a}}{\lambda}} \tag{3}$$

In Eq. (3), Δ is the width of fluctuations in distances between the neighboring scattering units and $\bar{a}$ (= $2\pi/q_\mathrm{m}$, where q_m is the value of the scattering vector corresponding to the peak maximum) is the characteristic size of the ordered elements. The interaction radius is a parameter that is defined by the region where the distribution function becomes practically smooth and approaches the mean value. “Gas”-type scattering with no maximum in the scattering curve occurs if the degree of disorder $\Delta/\bar{a}$ exceeds 0.25 - 0.3, whereas for $\Delta/\bar{a} \approx 0.2$ one already observes a strong first maximum. Formally speaking, reduction in $\Delta/\bar{a}$ would lead to the crystalline lattice; however, only high values of this parameter are characteristic for real objects.[14]

Results and disccusion

The scattering curves obtained in pure NaPSS and in mixed NaPSS/DPC and NaPSS/CPC solutions are shown in Figures 1a and 2a. The curves with S/P = 0.9 and 1.5 for DPC and with S/P = 1.0 and 1.3 for CPC correspond to a milky solution of the complex and to the precipitated 1:1 complex, respectively. The scattering pattern for pure NaPSS in water displays a smooth decay over the whole *q*-range studied. After the addition of surfactant to the polyelectrolyte, a broad diffraction maximum emerges in the curves, which becomes noticeably sharper for S/P values close to or higher than 1. For NaPSS/CPC complexes with S/P = 1 and 1.3, the scattering pattern even exhibits a very intense main peak accompanied by two well-resolved higher order peaks. This is shown in more detail in Figure 3 on a semi-logarithmic plot. One has to note that in pure DPC or CPC solutions in a similar concentration range of surfactant as studied in the mixed polyelectrolyte-surfactant systems (the highest total surfactant concentration in this study is around 2.2 vol %) no maximum was found.[6,7] In the case of pure surfactant solutions, a scattering peak occurs only for sufficiently high surfactant concentrations; typically, that is in a 10 vol % DPC or CPC solution,[6,7] at the *q*-value corresponding to the most

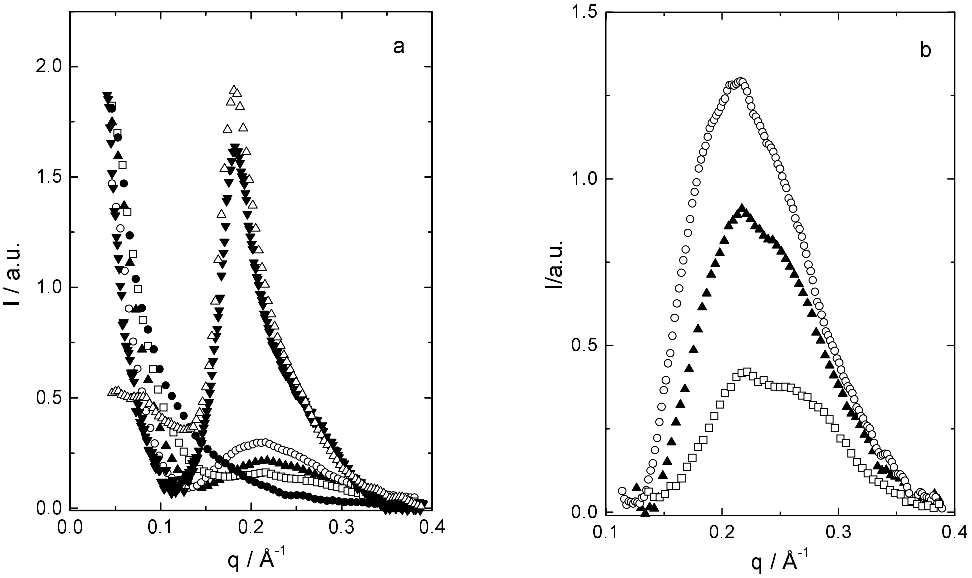

Figure 1. a) SAXS patterns for pure 1% NaPSS (●) and for NaPSS/DPC complexes with increasing S/P ratio: S/P = 0.3 (□), 0.5 (▲), 0.7 (○), 0.9 (▼), and 1.5 (Δ). **b)** the scattering in the region of the interference maximum, after subtracting the background, for solutions with S/P = 0.3, 0.5, and 0.7.

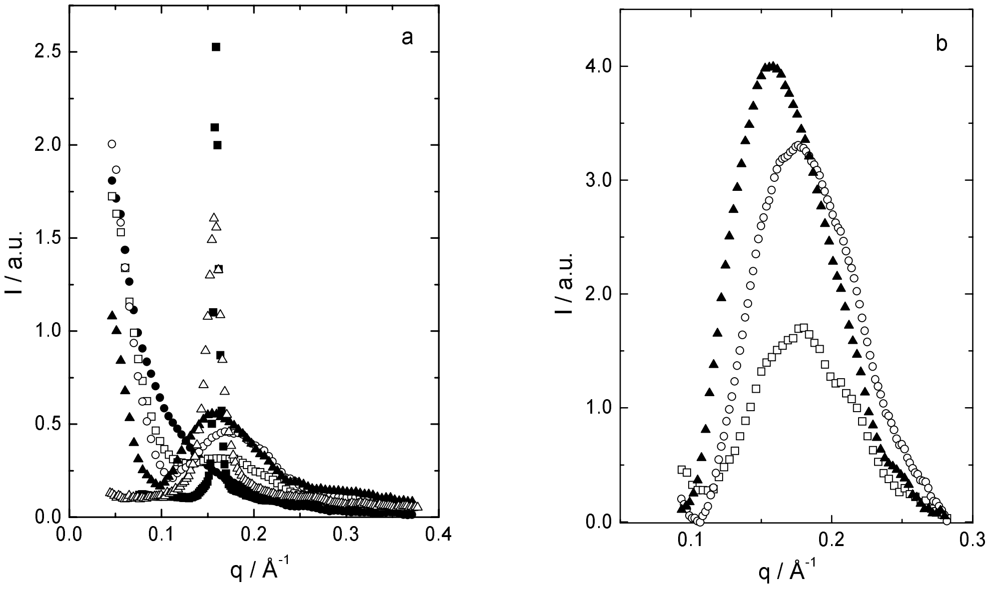

Figure 2. a) SAXS patterns for pure 1% NaPSS (●) and for NaPSS/CPC complexes with increasing S/P ratio: S/P = 0.3 (□), 0.5 (○), 0.7 (▲), 1.0 (Δ), and 1.3 (■). **b)** the scattering in the region of the interference maximum, after subtracting the background, for solutions with S/P = 0.3, 0.5, and 0.7.

probable distance d (= $2\pi/q_m$) between free surfactant micelles.

Figures 1b and 2b show the interference maxima for NaPSS/DPC and for NaPSS/CPC solutions, respectively, with S/P≤0.7 after subtracting the background. The maxima for complexes with higher S/P values retain their original shape after the correction for the background scattering. These will be treated later. The peak positions in q_m-values, the corresponding distances $\bar{a}$, and the structural parameters obtained from Eqs. 1-3 are reported in Table 1. In the NaPSS/DPC case, the peaks are found in the range of q_m-values from 0.243 to 0.19 Å^{-1}, whereas for NaPSS/CPC solutions they appear in the q_m-range from 0.178 to 0.157 Å^{-1}. One can see, that the increase in S/P-ratio causes the peak to shift to lower q_m-values. Consequently, the characteristic size of the ordered elements ($\bar{a}$) increases from 25.8 Å to 33.1 Å and from 35.2 Å to 38 Å for DPC (all S/P-values) and CPC (S/P ≤0.7), respectively. According to Tanford,[16] the lengths of extended dodecyl (C_{12}) and cetyl (C_{16}) chains embedded in a micellar core are 15.42 and 20.48 Å, respectively. Therefore, the reported $\bar{a}$-spacing-values are lower than or comparable to the largest possible extension of two C_{12} or C_{16} hydrocarbon chains incorporated in a liquid hydrocarbon-like environment, for example in a micellar core. These results suggest that DPC and CPC bind to the PSS anion in the form of micelles, which are smaller in size than micelles formed in pure detergent solutions. One

Table 1. Structural parameters of NaPSS/DPC and NaPSS/CPC complexes in water obtained from the peak(s) in the SAXS curves.

system	S/P	q_m / Å^{-1}	$\bar{a}$ / Å	L / Å	r_m / Å	$\Delta/\bar{a}$
NaPSS/DPC	0.3	0.243	25.8	52	82	0.22
	0.5	0.231	27.3	64	101	0.21
	0.7	0.222	28.4	67	106	0.21
	0.9	0.193	32.6	107	170	0.18
	1.5	0.190	33.1	118	186	0.16
NaPSS/CPC	0.3	0.178	35.2	90	142	0.20
	0.5	0.173	36.3	88	138	0.20
	0.7	0.165	38.0	92	159	0.20
	1.0 (peak 1)	0.157	40.1			
	1.0 (peak 2)	~0.257	24.4			
	1.0 (peak 3)	0.312	20.2			
	1.3 (peak 1)	0.159	39.5			
	1.3 (peak 2)	0.274	22.9			
	1.3 (peak 3)	0.317	19.8			

could propose that the reported $\bar{a}$-spacing is the centre-to-centre distance between micelles consecutively bound to the polyion. It comprises one micellar diameter and the thickness of the polymer chain wrapped around it. The polyelectrolyte chain has the role of connecting the micelles together, thus forming an aggregate of aggregates. As shown previously,[17] the aromatic benzenesulfonate rings on the polystyrenesulfonate anion solubilize in the hydrocarbon-like interior of the micellar aggregate. This specific interaction between the PSS chain and the aggregated surfactant leads to the "squeezing" of the micelle. The increase of $\bar{a}$ with increasing S/P ratio can be explained by the growth of micelles bound to the polyion, that is, by the increase of their aggregation number, whereas the number of micelle-like aggregates per polymer chain remains nearly constant. In accordance with this interaction scheme, the structural parameters L, r_m, and $\Delta/\bar{a}$ are fairly constant up to S/P = 0.7. So is the degree of disorder $\Delta/\bar{a}$, which is in the range from 0.22 to 0.2. According to Vainshtein,[15] the latter values lie on the boundary between the liquid-type scattering with at least one peak in the scattering curve and gas-type scattering where no peak is observed.

For complexes with S/P close to or higher than 1, a decrease in $\Delta/\bar{a}$ values is found (sharp peaks, see above), which points to a more ordered situation. In the case of NaPSS/DPC complexes, this is a relatively small decrease (see Table 1) and could be a consequence of the coalescence of polyelectrolyte-surfactant aggregates when their net-charge is decreased. On the contrary, for NaPSS/CPC complexes a substantial decrease in $\Delta/\bar{a}$ is found. A very sharp main peak and two well-resolved higher order peaks indicate this (see Figure 3). The q_m-values and the corresponding $\bar{a}$-spacings for these peaks are also given in Table 1. The L and r_m values increase considerably (for more than 10-times in comparison with complexes of lower S/P values), whereas the degree of disorder becomes considerably smaller than 0.1. It has been stated before that one cannot encounter extremely low values of $\Delta/\bar{a}$ (high values of L and r_m) in a real system; therefore, these values are not given in Table 1. Still, they are an indication of an essential increase in ordering, that can finally result in a crystalline-like organization of surfactant. The calculated $\sin^2\theta$ values for these peaks correspond to the sequence 1:3:4 (or in

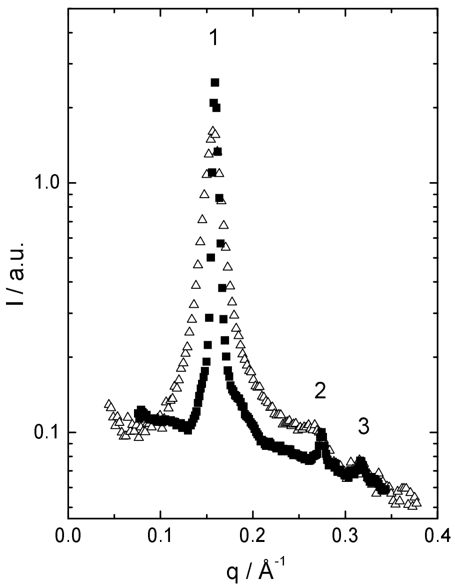

Figure 3. SAXS pattern for the NaPSS/CPC complex with S/P = 1.0 and 1.3 (symbols are the same as in Fig. 2a). The peaks are designated by numbers 1, 2, and 3 (for peak positions see Table 1).

q_m-values to the sequence 1:1.72:2) and indicate a hexagonal close-packed arrangement[18] of surfactant in the complexes. The unit cell dimension is equal to 39.5 Å (approximately one micellar diameter). It has been mentioned[5] that there is a tendency of a growth of micelle-aggregates into a rod-like or even cylindrical shape at sufficiently high surfactant concentrations. Therefore, one can propose that CPC in the precipitate with NaPSS is aggregated into long cylindrical micelles connected with polystyrenesulfonate chain into a very compact hexagonal phase. This is an often-encountered structure in the phase diagrams of pure surfactant-water systems[19] and a similar hexagonal structure has been recently reported for the arrangement of sodium dodecylsulfate in the cross-linked gels of poly(diallylmethylammonium chloride).[20]

One can conclude that the rather flexible and somewhat hydrophobic polystyrenesulfonate chain is intimately associated with an oppositely charged surfactant. Irrespective of the size of the surfactant tail, a typical aggregate with the PSS chain can be visualized as a complex where several micelles are surrounded by the polyion charges in such a way that some of the aromatic rings are embedded in the micelle surface. This could lead to a smaller size of the micelle-aggregate. The structural parameters show that the ordering is more pronounced in complexes with DPC than in the ones with CPC. When the charge of the PSS ion is completely neutralized by the surfactant (this only takes place with the longer-chain surfactant CPC) a hexagonal-close packed structure develops. In pure surfactant solutions, a hexagonal phase can be found at considerably higher detergent concentrations. Obviously, the PSS anion effectively "concentrates" the surfactant.

Acknowledgments

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Povzetek

Sipanje X-žarkov (izvor sinhrotron) smo uporabili za strukturne raziskave v sistemih natrijevega polistirenesulfonata (NaPSS) in dodecil- (DPC) in cetilpiridinijevega klorida (CPC) pri različnih molskih razmerjih med surfaktantom in polielektrolitom (S/P). Iz Braggovih maksimumov v sipalnih krivuljah smo predlagali dva tipa organizacije surfaktanta v povezavi s poliionom. V NaPSS/DPC (vse S/P vrednosti) in NaPSS/CPC kompleksih ($S/P\leq0.7$) je surfaktant agregiran v sferične micele, ki jih inducira poliion. Te micele so manjše od običajnih. Z večanjem S/P razmerja njihova velikost raste, a število micelnih agregatov na verigo poliiona ostaja približno konstantno. V NaPSS/CPC oborini ($S/P\geq1$) smo opazili heksagonalno fazo z vrednostjo celične konstante 39.4 Å; tu micele postanejo cilindrične oblike. V kompleksih z DPC nismo opazili podobne kristalinične stukture.