

Mixtures of Cationic Polyelectrolyte and Anionic Surfactant Studied with Small-Angle Neutron Scattering

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Small-angle neutron scattering (SANS) data for solutions containing a highly charged cationic polyelectrolyte and an anionic surfactant are presented. The scattering data were obtained in pure D₂O, emphasizing the scattering from the polyelectrolyte, and in a H₂O/D₂O mixture that contrast matches the polyelectrolyte. In the absence of surfactant, a broad scattering peak due to the mesh size of the polyelectrolyte solution is the most characteristic feature. This peak moves to larger q -values (smaller distances) as the polyelectrolyte concentration is increased, as expected for a semidilute polyelectrolyte solution. Addition of a small amount of surfactant reduces and finally removes this peak. Instead a sharp diffraction peak appears at high q -values. This Bragg peak corresponds to a characteristic distance of 37–39 Å, and it is observed when either the polyelectrolyte or the surfactant is contrast matched by the solvent. Once this peak has appeared, its position does not change when the surfactant concentration is increased. The intensity of the peak grows, however, until a stoichiometric polyelectrolyte–surfactant complex has been formed. The Bragg peak remains in excess surfactant solution. These results are discussed in relation to the structure of the polyelectrolyte–surfactant aggregates and in connection with recent results from surface force and turbidity measurements using the same polyelectrolyte–surfactant pair.

Introduction

The association between polyelectrolytes and oppositely charged surfactants has been extensively studied, and many recent reviews and books covering different aspects can be found.^{1–7} Most of the studies on the subject are concerned with association in bulk solution. One rationale for this is the importance of polyelectrolyte–surfactant systems as rheology modifiers,^{7,8} gelation agents,⁹ and solubilizers for sparingly soluble substances such as dyes,^{10,11} perfume, or pollutants.^{12,13} More recently, the association between polyelectrolytes and surfactants at interfaces has gained an increased interest.^{14–31} The association between ionic surfactants and oppositely charged polyelectrolytes in bulk solution is primarily affected by electrostatic and hydrophobic forces.^{32–37} In particular, it is found that in bulk solution, the initial binding of a charged surfactant to an oppositely charged polyelectrolyte is electrostatically driven. At a higher concentration, a cooperative association takes place that also is driven by the hydrophobic interaction (mainly between the surfactant tails). The surfactant concentration at which this cooperative association step occurs, the critical association concentration (cac), is lower than the critical micelle concentration (cmc), and it decreases with increasing charge density of the polyelectrolyte. The architecture

of the polyelectrolyte, such as branching, cross-links, and chain stiffness, also influences the association behavior.^{38–40} The properties of polyelectrolyte–surfactant complexes can be characterized by a range of methods. For instance, electrophoretic mobility and turbidity measurements in dilute polyelectrolyte solutions show that the sign of the charge of the aggregates changes as the surfactant concentration is increased³⁰ and that the turbidity as a function of surfactant concentration shows a maximum that coincides closely with the point of zero mobility. The dispersed aggregates are stable when their net charge is sufficiently high, but they flocculate and sediment when their charge is low.³⁰ Dynamic light scattering measurements provide information on the overall hydrodynamic size of the aggregates and the second virial coefficient.^{25,41,42} Fluorescence quenching measurements give valuable information on the size of the hydrophobic domains,⁴³ whereas X-ray⁴⁴ and neutron scattering experiments⁴⁵ give information on the internal structure of the aggregates. The picture that emerges from the latter techniques strongly depends on the system under investigation. For instance, Cosgrove et al. studied complexes between gelatin and SDS⁴⁵ and concluded from SANS measurements that micelle-like structures were formed along the polyelectrolyte chain in a bead-and-necklace structure, i.e., a similar arrangement as for the well-characterized complexes formed between uncharged poly(ethylene oxide) and SDS.^{46,47} On the other hand, Antonietti and co-workers found by X-ray studies that several polyelectrolyte–surfactant complexes formed ordered mesomorphous phases with quite complex topology.^{44,48–51}

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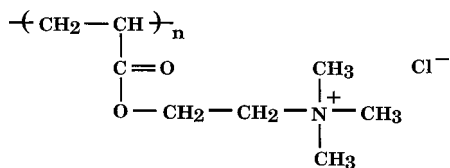


Figure 1. Chemical structure of poly{2-(propionyloxy)ethyl}-trimethylammonium chloride, PCMA.

Rather recently, various surface force techniques have been used to characterize structural forces in micellar solutions,^{52–55} in polyelectrolyte solutions,^{21,23,56,57} and between preadsorbed polyelectrolyte layers in the presence of surfactants.^{24,31} In all cases, oscillating forces that change from repulsion to attraction several times as the surfaces approach each other have been observed. The character of the oscillating forces measured between preadsorbed polyelectrolyte layers swelled by surfactants are, however, vastly different as compared to those observed in concentrated micellar solutions and in semidilute polyelectrolyte solutions. For instance, the force barriers are higher and the periodicity of the oscillations is smaller. They also appear despite that no polyelectrolytes are present in bulk solution (but only on the surfaces), and the surfactant concentration is below the cmc. Hence, it appears that different molecular mechanisms are responsible for the oscillating forces observed in the different experiments.

In the present study, we employ small-angle neutron scattering (SANS) to probe the structures of a semidilute polyelectrolyte solution of a highly charged cationic polyelectrolyte. In particular, we focus our attention on how addition of anionic surfactants affects the scattering curve. We use the data to shed some light on the structure of the polyelectrolyte–surfactant complexes formed. Note that away from charge stoichiometry, these complexes are dispersed in the aqueous phase. The information obtained proved valuable for increasing our understanding of the structural forces discussed above.

Materials and Methods

Materials. The polyelectrolyte used in this study was poly{2-(propionyloxy)ethyl}trimethylammonium chloride, PCMA, with a mean molecular mass of 1.6×10^6 g/mol. Each monomeric segment of the polyelectrolyte carries one positive charge as shown in Figure 1. The polyelectrolyte was synthesized and kindly provided by the Laboratoire de Physico-Chimie Macromoléculaire, Université Pierre et Marie Curie, Paris. The surfactant, deuterated sodium dodecyl sulfate (SDS-*d*) was obtained from Isotec Inc. (lot no. EK2050-7) and used without further purification. D₂O was chosen as a solvent to minimize the incoherent background from hydrogen and to obtain a high scattering contrast with the PCMA while contrast matching the SDS-*d*. A mixture of 80 wt% H₂O and 20 wt% D₂O was used as a solvent to contrast match PCMA while yielding a high scattering contrast with SDS-*d*.

The average excess scattering length density, $\Delta\rho$, was calculated using the appropriate molecular volumes and weights of the surfactant monomers [$\Delta\rho_{\text{SDS-}d}(\text{D}_2\text{O}) = 0.33 \times 10^{10} \text{ cm}^{-2}$ for SDS-*d* in D₂O, $\Delta\rho_{\text{SDS-}d}(\text{mix}) = 5.90 \times 10^{10} \text{ cm}^{-2}$ for SDS-*d* in a 80/20 H₂O/D₂O mixture, $\Delta\rho_{\text{PCMA}}(\text{D}_2\text{O}) = -5.44 \times 10^{10} \text{ cm}^{-2}$ for PCMA in D₂O and $\Delta\rho_{\text{PCMA}}(\text{mix}) = 0.13 \times 10^{10} \text{ cm}^{-2}$ for PCMA in a 80/20 H₂O/D₂O mixture].

Methods. The SANS experiments were performed at the D11 SANS instrument at Institut Laue-Langevin (ILL), Grenoble, France. A range of scattering vectors q from 0.003 to 0.2 Å^{−1} was covered by three sample-to-detector distances (1.2, 5.5, and 12 m) at the neutron wavelength 8 Å. The setting with a 5.5 m

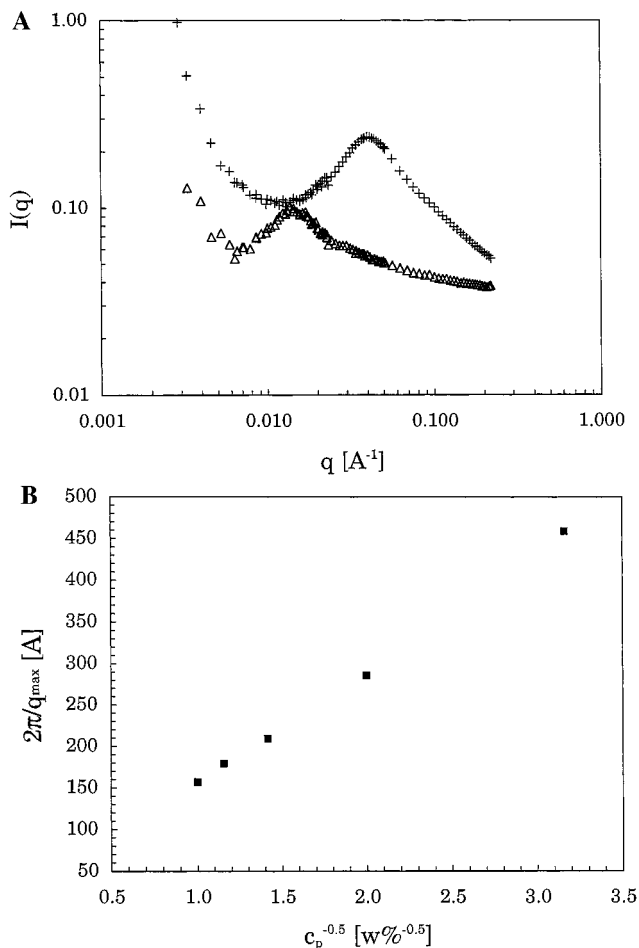


Figure 2. (A) Scattering intensity as a function of scattering vector for PCMA samples in D₂O. The PCMA concentrations were 0.1 wt % (Δ) and 1% (+). (B) Characteristic distance ($= 2\pi/q_{\text{max}}$) as a function of the inverse square root of the PCMA concentration in D₂O.

sample-to-detector distance was used as the reference setting for the absolute scale. The wavelength resolution was 10% (full width at half-maximum value).

The samples were kept in quartz cells (Hellma) with a path length of 2 mm for samples in D₂O, whereas 1-mm cells were used for samples in the solvent mixture 80 wt% H₂O and 20 wt% D₂O. The raw spectra were corrected for background from the solvent, sample cell, and other sources by conventional procedures.⁵⁸ The two-dimensional isotropic scattering spectra were azimuthally averaged, converted to an absolute scale after being corrected for detector efficiency by dividing by the incoherent scattering spectra of pure water measured in a 1-mm cell.⁵⁹

Results

The polyelectrolyte PCMA forms an isotropic and clear solution with water. The scattering behavior of samples containing pure polyelectrolyte at two different concentrations in D₂O is shown in Figure 2A. For the 0.1 wt % PCMA solution, a clear peak at $q \approx 0.013\text{--}0.014 \text{ Å}^{-1}$ is observed. The position of the peak is displaced toward higher q -values ($q \approx 0.04 \text{ Å}^{-1}$) when the polyelectrolyte concentration is increased to 1 wt%. The peak corresponds to a characteristic distance ($\sim 2\pi/q_{\text{max}}$) in the polyelectrolyte solution that decreases from about 460 Å to about 160 Å when the concentration is increased by a factor of 10. The peaks are rather broad as a result of a comparatively large standard deviation in the distribution of distances between the structural units. The scattering curves for 0.25, 0.5, 0.75 wt

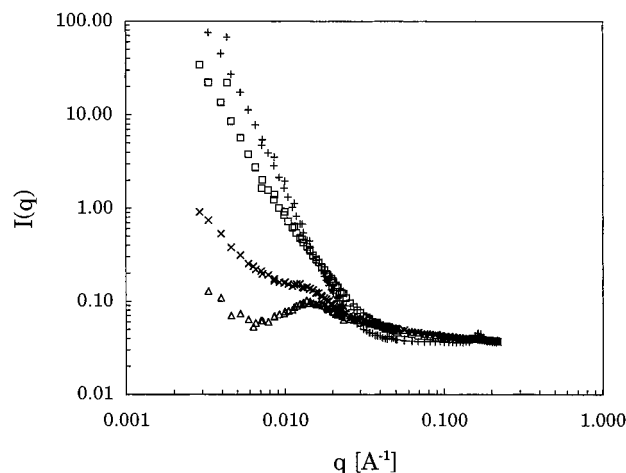


Figure 3. Scattering intensity as a function of scattering vector for a 0.1 wt % PCMA solution in D₂O. The SDS-*d* concentration was 0 (Δ), 0.005 wt % ($r = 0.03$, \times), 0.05 wt % ($r = 0.3$, \square), and 0.5 wt % ($r = 3$, $+$).

% looked qualitatively similar as those presented in Figure 2A with peak positions at 0.022, 0.03, and 0.035 Å⁻¹, respectively. Figure 2B shows the characteristic distance as a function of the inverse square root of the polyelectrolyte concentration.

The polyelectrolyte surfactant mixture was obtained by adding a small amount of a concentrated polyelectrolyte solution to the surfactant solution under stirring. In a certain concentration range, the solution becomes cloudy and large objects can be seen with the naked eye. Some aggregates remain dispersed in the aqueous phase whereas others precipitate. Away from charge stoichiometry the dispersed aggregates are quite stable (particularly at low polyelectrolyte concentrations), whereas a rapid sedimentation occurs when the ratio of SDS to charged segments is close to one. Hence, the scattering data after addition of sufficient SDS-*d* is obtained in a two-phase system consisting of aggregates with a high concentration of polyelectrolyte and surfactant dispersed in an aqueous solution containing a low concentration of free surfactant. The amount of precipitate under our measuring conditions was zero or small. Hence, the scattering comes from the dispersed aggregates. The scattering length density for SDS-*d* relative to the D₂O solvent, $\Delta\rho_{\text{SDS-}d}(\text{D}_2\text{O}) = 0.33 \times 10^{10} \text{ cm}^{-2}$, is negligible as compared to the corresponding quantity for the polyelectrolyte [$\Delta\rho_{\text{PCMA}}(\text{D}_2\text{O}) = -5.44 \times 10^{10} \text{ cm}^{-2}$], and hence, only the PCMA, and not the SDS-*d*, contributes to the scattering for samples where pure D₂O is used as a solvent. Moreover, the sulfate headgroup has a scattering length density very similar to D₂O⁶⁰ so that both head and tail of SDS-*d* is contrast matched in pure D₂O. When 0.005 wt % SDS-*d* (the ratio SDS-*d*/charged segments, $r = 0.03$) is admixed into the solutions where 0.1 wt % polyelectrolyte is dissolved in pure D₂O, the peak at 0.013–0.014 Å⁻¹ becomes less pronounced. A further increase in SDS-*d* concentration leads to a complete disappearance of this peak (cf. Figure 3). Instead, a new sharp peak appears at $q \approx 0.16\text{--}0.17 \text{ Å}^{-1}$. The intensity of this peak, which is emphasized in Figure 4, increases with increasing surfactant concentration, but the position remains unaltered. The position of the peak corresponds to a characteristic distance of 37–39 Å.

In a mixture of 80 wt% H₂O and 20 wt% D₂O, the polyelectrolyte is contrast matched [$\Delta\rho_{\text{PCMA}}(\text{mix}) \approx 0$] so that only SDS-*d* [$\Delta\rho_{\text{SDS-}d}(\text{mix}) = 5.9 \times 10^{10} \text{ cm}^{-1}$] contributes to the scattering intensity. The scattering data for SDS-*d* in 0.1 wt % solutions of PCMA in the 80/20 H₂O/D₂O mixtures are given in Figure 5 for different concentrations of SDS-*d*. The

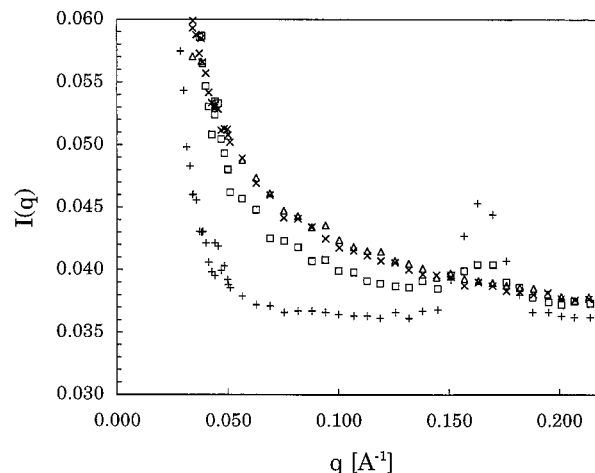


Figure 4. Scattering intensity at high q -values as a function of scattering vector for a 0.1 wt % PCMA solution in D₂O. The SDS-*d* concentration was 0 (Δ), 0.005 wt % ($r = 0.03$, \times), 0.05 wt % ($r = 0.3$, \square), and 0.5 wt % ($r = 3$, $+$).

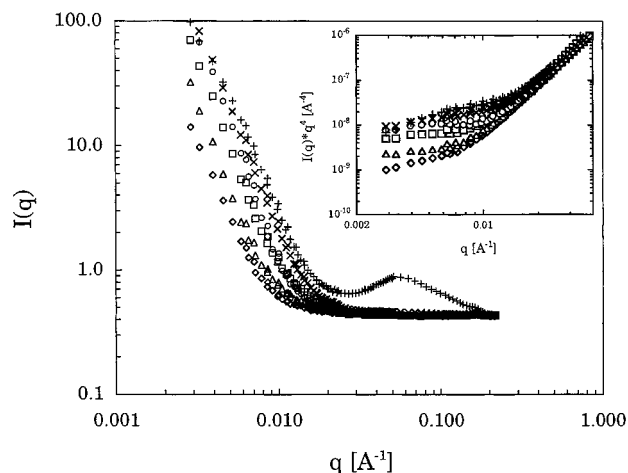


Figure 5. Scattering intensity as a function of scattering vector, q , for a 0.1 wt % PCMA solution in an H₂O/D₂O (80/20) mixture. The SDS-*d* concentration was 0.02 wt % ($r = 0.12$, \diamond), 0.05 wt % ($r = 0.3$, Δ), 0.1 wt % ($r = 0.6$, \square), 0.2 wt % ($r = 1.2$, \circ), 0.5 wt % ($r = 3$, \times), and 2 wt % ($r = 12$, $+$). The inset shows $I(q)q^4$ as a function of q . The plots become constants at low q values indicating a three-dimensional structure of the aggregates.

scattering intensity at low q -values increases with increasing SDS-*d* concentration, and the slope of the scattering curve below q about 0.007 Å⁻¹ decreases roughly as $\propto q^{-4}$ indicating that the objects are three-dimensional structures at distances larger than about 900 Å. They can most certainly be identified with the aggregates in solution. We note, however, that the scattering curve at 0.2 wt % SDS-*d* ($r = 1.2$), which is the one closest to charge stoichiometry, is distinctly nonlinear on a log–log scale also for q -values below 0.01 Å⁻¹. For the highest SDS-*d* concentration (2 wt %, $r = 12$), a peak corresponding to the presence of free SDS-*d* micelles is clearly seen at $q = 0.05\text{--}0.06 \text{ Å}^{-1}$. Assuming that all charges of the PCMA is compensated by SDS-*d* and considering that the cmc for SDS-*d* is about 0.26 wt % gives a concentration of free micelles of 1.6 wt %. A peak located exactly at this position has been observed in SANS data for samples containing pure SDS micelles,⁶⁰ which supports our conclusion that its origin is free SDS-*d* micelles coexisting with the surfactant dressed PCMA chains. The peak in the scattering curve for this particular sample is due to repulsive double-layer interactions between the charged micelles.

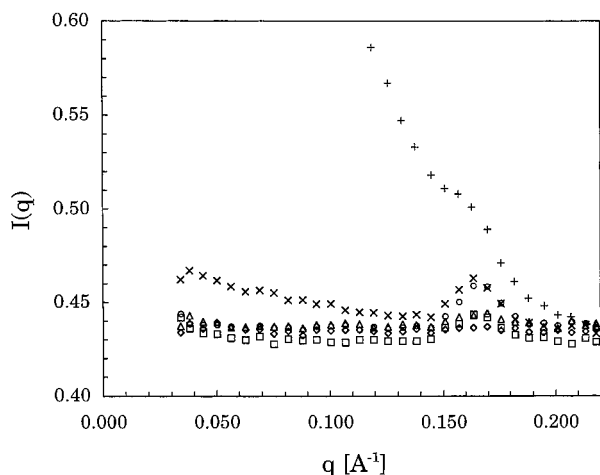


Figure 6. Scattering intensity as a function of scattering vector at high q -values for a 0.1 wt% PCMA solution in an $\text{H}_2\text{O}/\text{D}_2\text{O}$ (80/20) mixture. The SDS- d concentration was 0.02 wt% ($r = 0.12$, ◇), 0.05 wt% ($r = 0.3$, △), 0.1 wt% ($r = 0.6$, □), 0.2 wt% ($r = 1.2$, ○), 0.5 wt% ($r = 3$, ×), and 2 wt% ($r = 12$, +).

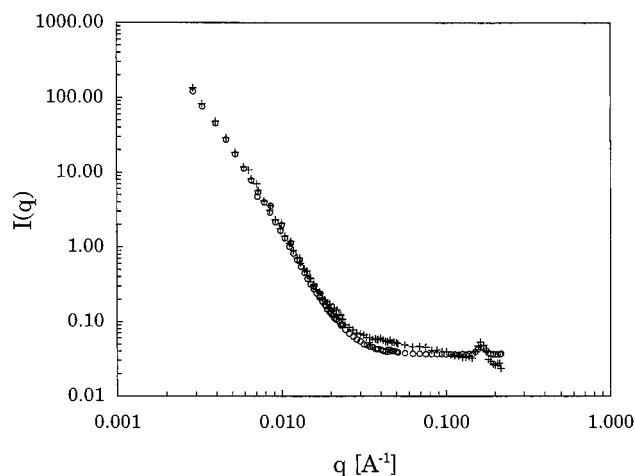


Figure 7. Scattering intensity as a function of scattering vector for a solution of 0.1 wt% PCMA and 0.5 wt% SDS- d in D_2O (○) and a 80/20 mixture of H_2O and D_2O (+).

Another important finding is that, similar to the corresponding solutions where pure D_2O was used as a solvent, a peak located at $q \approx 0.16\text{--}0.17 \text{ \AA}^{-1}$, the intensity of which increases with increasing SDS- d concentration, is found for each sample, (Figure 6). Hence, we may conclude that the SDS- d interacts with parts of the polyelectrolyte chains so as to form a common structure that contributes similarly to the behavior of the scattering data at high q -values for samples in which either the polyelectrolyte or the oppositely charged surfactant is contrast matched. This is further emphasized by the data in Figure 7, which illustrate the complete scattering curve for the solutions containing 0.1 wt % PCMA and 0.5 wt % SDS- d ($r = 3$) determined in D_2O (emphasizing the scattering from the polyelectrolyte) and in the 80/20 $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture (showing the SDS- d). The small difference that is observed at intermediate scattering vectors is attributed to the presence of some free SDS- d micelles, the concentration of which is estimated to be 0.08 wt %.

Discussion

Structure of Polyelectrolyte Solutions. The knowledge about the organization of polyelectrolyte solutions has increased during the last years. However, as discussed in a recent review article

by Förster and Schmidt⁶¹ many unresolved issues remain. The key features of polyelectrolyte solutions arise due to the large repulsive force between the macroions that tends to keep them apart. The strong intrachain repulsion forces the polyelectrolytes, that on average contains 8000 charged segments, to adopt stretched conformations. The intra- and interchain repulsion is decreased with increasing ionic strength.

The polyelectrolyte solutions investigated are in the semidilute regime. In such cases, it is often observed that the characteristic distance, as e.g., measured with SANS, varies linearly with $1/\sqrt{c_p}$, where c_p is the concentration of polyelectrolyte.⁶¹ This relation has been plotted in Figure 2B, and it can be seen that all points with good approximation indeed lie on a straight line. The numerical values of the characteristic distances are also in excellent agreement with the data presented by Kaji et al. for sodium polystyrenesulfonate.⁶² The data presented here can be interpreted as the mesh size ($= 2\pi/q_{\text{max}}$) of the polyelectrolyte network.^{23,61}

Interestingly, we note that addition of a small amount of SDS- d to the 0.1 wt % PCMA solution removes the peak in the scattering curve. This occurs at a ratio of surfactant to polyelectrolyte charges of between 0.03 and 0.3 (Figure 3). This corresponds to, at the higher concentration, an increase in ionic strength by about 30%. Hence, the observed effect is hardly due to an increase in ionic strength and thus a decrease in the Debye-length. The ratio of SDS- d to polyelectrolyte segments is only 0.03 at the lowest SDS- d concentration (Figure 3), and already at this point the scattering at low q -values has increased significantly rendering it more difficult to identify the peak describing the mesh size in the scattering curve. The most plausible interpretation is that the large interacting polyelectrolyte-surfactant complexes contribute significantly to the scattering at low q -values, thus rendering it more difficult to observe the correlation peak.

Oscillating Forces due to the Structure of Polyelectrolyte Solutions. Recently, some investigations of oscillating forces between solid surfaces or air-liquid interfaces immersed in micellar surfactant solutions and in semidilute polyelectrolyte solutions have been reported. The structural forces in micellar solutions have been identified as arising from changes in the structure of the solution confined between the interfaces.^{52,54,55} In bulk, the charged micelles are repelled from each other due to repulsive interactions. In the confined space between the interfaces, the mean distance between the aggregates is different as compared to in bulk solution. As the film thickness decreases, it becomes favorable to displace some of the aggregates from the thin film to bulk rather than decreasing the mean distance between them further. This is the origin of the oscillating structural force.

Similarly, an oscillating force arises in semidilute polyelectrolyte solutions due to a rearrangement of the structure due to the confinement.^{21,23,56,57} The periodicity of the oscillations compares favorably with the mesh size found in bulk polyelectrolyte solutions,²³ and the molecular origin for the oscillating structural force observed in this case thus seems clear. However, as pointed out by Klitzing et al.,⁵⁷ it is more difficult to fully understand the rearrangement that gives rise to the oscillating force in this case.

Internal Structure of Polyelectrolyte-Surfactant Aggregates. The SANS data presented here shed some light on the internal structure of the aggregates formed by PCMA and SDS- d . The most important piece of information comes from the Bragg diffraction peak observed at q -values $= 0.16\text{--}0.17 \text{ \AA}^{-1}$. This peak corresponds to a distance of 37–39 Å, and it is

present both when either the surfactant or the polyelectrolyte is contrast matched. This means that both polyelectrolyte segments and surfactant molecules build up this structure and that the characteristic distance for both components is the same. We note that when more SDS-*d* is added (below the charge neutralization point) the peak grows in intensity, but its position is unaffected. Thus, a larger fraction of the polyelectrolyte chains adopts the preferred structure as the charge neutralization point is approached. A consequence of this is that below the charge neutralization point the surfactants are unevenly distributed among and/or along the polyelectrolyte chains. However, no scattering peak similar to that observed for free SDS micelles⁶⁰ or for SDS micelles bound to poly(ethylene oxide)^{46,47} is observed. Thus, the bead-and-necklace model does not describe the structure formed. Our data are not sufficient to provide a detailed structural picture of the complex. For this data at higher *q*-values would be needed, but it seems very likely that the internal structure of the aggregates is similar to the mesomorphic polyelectrolyte-surfactant phases characterized by Antonietti and co-workers.^{44,48–51} In accordance, SDS-*d* forms closely packed lamellar bilayers that are divided by aqueous layers where the polyelectrolyte is located together with the surfactant headgroups. The possibility that SDS-*d* forms cylinders packed in a hexagonal pattern, rather than bilayers, cannot, however, be excluded from our SANS data.

We emphasize that the Bragg peak is present at the same position even when the SDS-*d* concentration is much larger than the polyelectrolyte segment concentration. Hence, the stoichiometry of the structural units is not significantly changed, since a significant charge imbalance (due to excess SDS-*d* within the structure) would lead to a strong swelling due to repulsive double-layer forces. On the other hand, measurements of the mobility of the aggregates in excess SDS show that they have obtained a significant negative charge.³⁰ Taken together, these results imply that the excess SDS, that gives rise to the net negative charge, is located on the surface of the aggregates. The picture that emerges is that of rather close packed aggregates where the center of the surfactant dressed polyelectrolyte chains in the interior are separated by 37–39 Å, whereas the surface of the aggregates carries a net charge. The charge is positive, due to excess segments at the surface below the charge neutralization point, whereas the excess surfactants at the surface gives the aggregates a net negative charge at high surfactant concentrations.

Oscillating Forces due to Structures of Adsorbed Polyelectrolyte-Surfactant Layers. Force measurements have shown that when preadsorbed layers of PCMA are swelled with SDS an oscillating force profile is obtained. One example of such a force curve, measured across a submicellar SDS solution, is shown in Figure 8. Several oscillations are observed. The magnitude of both the repulsive and the attractive branches increases with decreasing separation, whereas the periodicity remains the same, about 40 Å. Similar force curves, with the same periodicity, have been observed in the SDS concentration range 0.2–2 cmc.^{24,26} The same characteristic distance has also been observed in AFM force measurements and AFM-images of the preadsorbed PCMA layer in the presence of SDS.³¹ The similarity between the characteristic distance describing the internal structure of PCMA-SDS complexes (37–39 Å) and the periodicity of the oscillating forces presented in Figure 8 provide strong support to the view that they have the same molecular origin. Alternative interpretations based on bulk structures can in this case be dismissed because no polyelectrolytes are present in solution during the force measurement

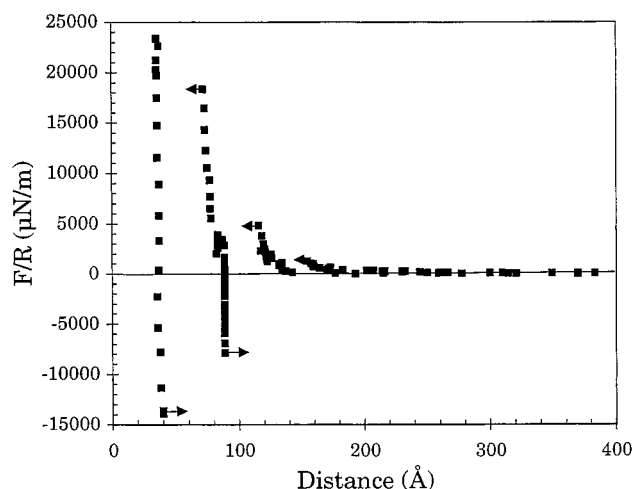


Figure 8. Force normalized by radius as a function of separation between two mica surfaces precoated with a layer of PCMA. The solution contains 4.1 mM SDS (0.5 × cmc) but no polyelectrolytes (■).

and because the surfactant concentration is submicellar. Thus, these structural forces arise due to the structure of the adsorbed layer rather than due to structures in the bulk solution. The SANS data presented in the present paper also show that the bead-and-necklace model originally proposed to describe the oscillating force profile is incorrect,²⁴ but rather structures similar to those characterized by Antonietti and co-workers^{44,48–51} are consistent with the data.

Conclusions

The scattering data for semidilute surfactant-free PCMA solutions in D₂O show a broad peak corresponding to a relatively large characteristic distance describing the mesh size. This distance decreases as the polyelectrolyte concentration increases consistent with results reported for other polyelectrolyte solutions. The peak, however, rapidly vanishes as an increasing amount of the anionic surfactant SDS-*d* is added to the PCMA solutions, and, instead, a sharp correlation peak is displayed corresponding to a significantly smaller and more well-defined characteristic distance of 37–39 Å. The same characteristic distance is obtained for both the polyelectrolyte chain and the surfactant. This is consistent with the formation of aggregates consisting of polyelectrolyte chains that, at charge stoichiometry, are evenly dressed with SDS-*d*. In this arrangement, the electric charges on the PCMA are canceled by SDS-*d*, which makes it possible for the dressed chains to be packed close together within an overall three-dimensional aggregate structure as indicated by the $I \propto q^{-4}$ behavior at low *q* values. The characteristic distance that describes the internal structure of the aggregates agrees nicely with the characteristic periodicity in the force curve between surfaces precoated with PCMA and then exposed to SDS, and they reflect the same structure. Further, in excess SDS, the aggregates obtain a net negative charge, whereas the characteristic distance describing the internal structure of the aggregates is unaffected. This demonstrates that the excess surfactant is located at the surface of the aggregate.

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