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Role of the Preparation Procedure in the Formation of Spherical and Monodisperse Surfactant/Polyelectrolyte Complexes

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Abstract: Complexes formed by a double-tail cationic surfactant, didodecyldimethyl ammonium bromide, and an anionic polyelectrolyte, an alternating copolymer of poly(styrene-alt-maleic acid) in its sodium salt form, were investigated with respect to variation in the charge ratio (x) between the polyelectrolyte negative charges and the surfactant positive charges. The morphology and microstructure of the complexes were studied by light microscopy and small-angle X-ray scattering for different preparation conditions. Independent of the sample preparation procedure and the charge ratio x, the X-ray results show that the microscopic structure of the complexes is a condensed lamellar phase. By contrast, the morphology of the complexes changes dramatically with the preparation procedure. The complexes formed by mixing a surfactant solution and a polyelectrolyte solution strongly depend on x and are always extremely heterogeneous in size and shape. Surprisingly, we show that, when the two solutions interdiffuse slowly, spherical complexes of micrometric and rather uniform size are systematically obtained, independently on the initial relative amount of surfactant and polyelectrolyte. The mechanism for the formation of these peculiar complexes is discussed.

Keywords: amphiphiles · electrostatic interactions · polyelectrolytes · self-assembly · surfactants

Introduction

The interactions between surfactants and polymers have been widely investigated due to their numerous applications from the daily life to the various industries (e.g. pharmaceutical, biomedical application, detergency, enhanced oil recovery, paints, and food and mineral processing).[1–3] However, most of the studies focused on the structure of the aggregates made of surfactants and neutral polymers[4–10] or charged surfactants and oppositely charged polyelectrolytes in dilute solution, that is, systems in which phase separation does not occur.[11–15] The general picture about the interaction between surfactant and polyelectrolyte emerging from these studies is that the surfactant molecules adsorb on polyelectrolyte chains as micellar or micelle-like clusters.[11] Over the last two decades, the complexes formed by charged surfactants and oppositely charged polyelectrolytes have been a focus of scientific research due to their potential application in polymer and biomedical science.[16–21] Substantial efforts have been made to clarify the structures of the polyelectrolyte–surfactant complexes in more concentrated solutions and it has been found that, very generally, the structure of the complexes exhibits a long-range order reminiscent of the structures classically found in surfactant/water solution.[22–26] We note that the concentration of polyelectrolyte has a major effect on the behavior of oppositely charged surfactant bilayers at a mesoscopic scale. Diluted polyelectrolyte solution induces a peeling of the successive surfactant bilayers that constitute a multilamellar vesicle,[27] while a more concentrated polyelectrolyte solution induces novel structural transitions of the charged surfactant bilayers.[28] Notable studies by other groups include, in particular, the work of Berret et al. who found that neutral/polyelectrolyte diblock copolymers and oppositely charged surfactants in aqueous solution associate into colloidal aggregates that have an original core-shell microstructure, with a core made up of by densely packed surfactant micelles connected by the polyelectrolyte blocks.[17] Numerous experimental investigations also deal with the interactions between cationic surfactants or lipids and DNA as the negative polyelectrolyte, due to its important application in gene therapy.[29–35] In

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particular, Kennedy et al. found that the order of addition of DNA to lipid or vice versa could affect the size and size distribution of the complexes.[34] Similarly, Boffi et al. showed that two distinct types of complexes are formed in the cationic liposome and DNA system.[35] The effect of sample preparation on the complexes is also mentioned for synthetic polyelectrolyte and surfactant.[36] However, stable uniform micrometer size complexes were never obtained in those studies.

In this paper, using light microscopy and small-angle X-ray scattering as analytical techniques, we study in detail the effect of the sample preparation procedures on the resultant morphology and structure of complexes formed by a bilayer-forming cationic surfactant and an anionic polyelectrolyte. The shape and size of the complexes can be directly observed under the light microscope, without particular sample preparation (such as drying, metal coating, etc.) as required for electron microscopy for instance, whereas X-ray scattering gives us information about the internal microscopic structure of the complexes. We show for the first time that the morphology of the complexes formed by the double-chain cationic surfactant and the negatively charged polyelectrolyte depends dramatically on the preparation procedure and that spherical complexes the size of which is rather uniform can be obtained under certain conditions. The mechanism of the formation of these peculiar complexes is briefly discussed at the end of the paper.

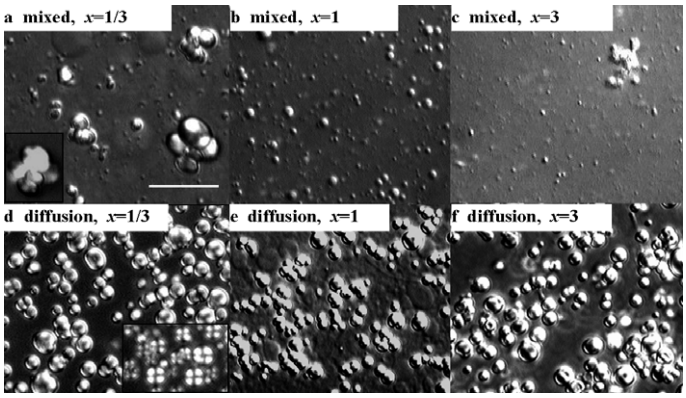

Figure 1. Light microscopy pictures of the polyelectrolyte/surfactant complexes obtained with the "mixing" (a–c) and "diffusion" (d–f) procedures, at different charge ratios (x). All pictures are taken in differential interference contrast except the insets of Figure 1a and 1d, which are taken between crossed polarizers. The scale bar represents 20 μm and is the same for all pictures. The final concentrations of surfactant and polyelectrolyte in the mixture are 0.84 % and 0.08 % (a, d), 0.64 % and 0.18 % (b, e), and 0.37 % and 0.32 % (c, f) in weight.

Results and Discussion

Morphology of the complexes formed with the "mixing" and "diffusion" procedures: The two sample preparation procedures, so called "mixing" and "diffusion", are described in detail in the Experimental Section. Briefly, in the "mixing" procedure, the surfactant solution and the polyelectrolyte solution are mixed together, while in the "diffusion" procedure, the two solutions are gently put into contact and are left to interdiffuse. Figure 1a–c shows the light microscopy pictures of the complexes formed by the negatively charged polyelectrolyte, an alternating copolymer of styrene and maleic acid in its sodium salt, and the cationic surfactant, didodecyldimethyl ammonium bromide (DDAB),by means of the "mixing" procedure for different charge ratio (negative/positive: $x=1/3$, 1, 3). Our observations are similar to what has been discussed previously.[27] Extremely polydisperse complexes are formed for all x. For instance, for $x=1/3$, the complexes size ranges from 0.8 to 14.7 μm. For $x\leq 1$, that is, in excess of surfactant, the complexes have a rather rounded shape, while their contour is more irregular for $x>1$, that is, in excess of polyelectrolyte. Vesicles and complexes coexist for $x=1/3$, while no pure surfactant vesicles can be detected for $x\geq 1$. Surprisingly, we found that the morphology of the complexes by "diffusion" procedure is markedly different from those formed with the "mixing" procedure. Figure 1d–f shows the light microscopy pictures of the complexes formed using the "diffusion" procedure, for charge ratio $x=1/3$, 1, and 3, respectively. As can be seen on these pictures, the complexes thus formed are spherical in shape and of rather uniform size (polydispersity of the order of 20 %). We note moreover that, as opposed to the "mixed" samples, the morphology of the complexes does not seem to depend on the charge ratio. We measure that their diameter is of the order of 2.9 ± 0.5 μm, irrespective of the charge ratio for the "diffusion" sample. When observed between crossed polarizers, these complexes exhibit a well-defined spherulite texture with a distinct Maltese cross, indicating the formation of a concentric and regular lamellar structure on a micrometer scale (inset in Figure 1d). This can be contrasted with the complexes formed in "mixed" samples, for which birefringence is detected (the complexes appear also bright between crossed polarizers), but no regular birefringent pattern is observed, indicating a lack of organization on a large length scale (see inset of Figure 1a).

We note that the complexes formed by means of the "diffusion" procedure are very stable when diluted in pure water as their structure has been maintained for more than nine months. They are also stable in the presence of additional cationic surfactant such as DDAB (0.5 % w/w) or cetylpyridinium chloride (0.5 % w/w). Additionally, we observed that they are also stable when put in a salt solution (NaBr) with a concentration smaller than 0.1 M, but are destabilized for higher salt concentrations (results not shown). Finally, we found that further addition of a negatively charged surfactant, such as sodium dodecyl sulfate (SDS), and of the negatively charged polyelectrolyte to a solution of complexes in water destabilize the complexes. As shown in Figure 2, upon addition of the negatively charged species, SDS (a) and polyelectrolyte (b), the spherical complexes are deformed and some large aggregates occur. We note in addi-

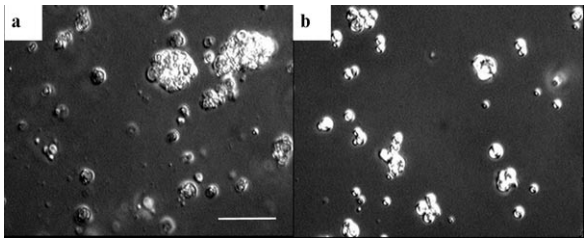

Figure 2. Morphology of the complexes formed with the "diffusion" procedure upon addition of a) SDS (0.053 % w/w) and b) polyelectrolyte (0.006 % w/w). The scale bar represents 20 μm and is the same for the two pictures.

tion that the complexes can be completely dissolved with addition of large amount of SDS or polyelectrolyte.

Microstructure of the complexes formed using the "mixing" and "diffusion" sample preparation procedures: To probe the internal microstructure of the complexes, small-angle X-ray scattering (SAXS) experiments were performed. Figure 3 shows the SAXS results for complexes formed

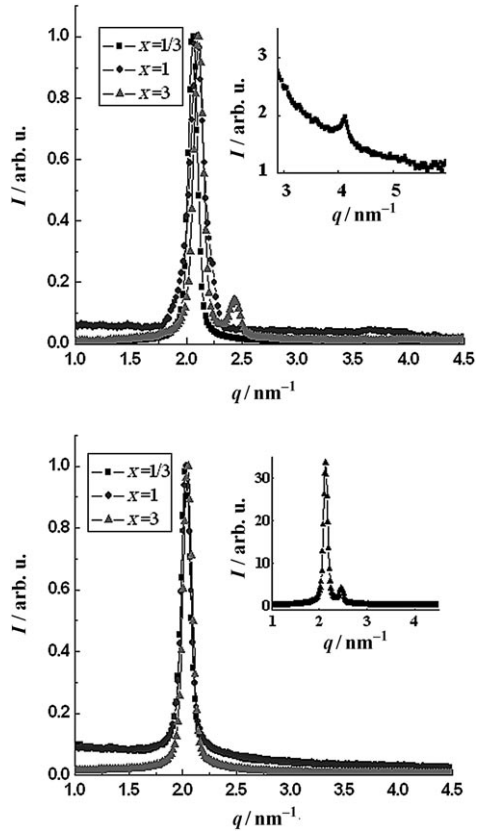

Figure 3. Small angle X-ray scattering results for the "mixed" (top) and "diffusion" (bottom) samples at different charge ratios ($x=1/3$, 1, and 3). The inset in the top panel is an enlarged image of the high q region for $x=1/3$, and the inset in the bottom panel is the result for a "diffusion" sample ($x=3$) after remixing. For all samples, the initial surfactant and polyelectrolyte concentrations are the same as those in Figure 1.

using the "mixing" and "diffusion" procedures, at different charge ratios. As described previously,[27] for the "mixed" samples, the SAXS patterns depend on the charge ratio. For $x \leq 1$, two peaks are observed at $q_0 \approx 2.06\ \mathrm{nm}^{-1}$ and $q_1 \approx 2q_0 \approx 4.12\ \mathrm{nm}^{-1}$ (the inset of Figure 3 (top) is the enlargement at large values of q, revealing the peak at q_1.). When $x > 1$, the SAXS pattern exhibits systematically three peaks at about $q_0 \approx 2.11\ \mathrm{nm}^{-1}$, $q^* \approx 2.44\ \mathrm{nm}^{-1}$, and $q_1 \approx 2q_0 \approx 4.06\ \mathrm{nm}^{-1}$. Hence, in addition to the peaks at q_0 and $2q_0$, another peak appears at $q^* \approx 1.2q_0$, the possible origin of which is discussed below.

By contrast, the SAXS patterns for the complexes formed with the "diffusion" procedure do not depend on the charge ratio (x) as shown in Figure 3 (bottom): irrespective of x, two peaks at q_0 and $q_1 \approx 2q_0$ are measured. Hence the SAXS spectra of these complexes are similar to those of the mixed samples for $x \leq 1$. These observations are rather robust: SAXS experiments for complexes prepared at other polyelectrolyte concentrations (0.1 %, 2 %, 15 % (w/w)) keeping $x=3$ were also carried out using the "mixing" and "diffusion" preparation procedures. We find that all SAXS patterns for the "mixed" samples display, in addition to peaks at q_0 and $2q_0$, a peak at $q^* \approx 1.2q_0$, while only two peaks at q_0 and $2q_0$ are detected in the "diffusion" samples. Moreover, we also find that the microstructure of the complexes does not depend on the surfactant concentration (c_s) in the range of c_s investigated (between 0.10 % and 1 % by weight). Interestingly, we moreover note that if we mix the "diffusion" sample (with $x=3$), once the equilibrium state has been reached (as shown in Figure 6d in the Experimental Section), the complexes loose their spherical and uniform morphology, and become similar to that of the "mixed" sample with a same x. This morphological change is accompanied by the occurrence of a peak at $q^* \approx 1.2q_0$ in the SAXS spectrum (inset Figure 3, bottom), a feature also similar to that of a mixed sample.

The occurrence of peaks at q_0 and $2q_0$ is the signature of a lamellar phase, which is in accordance with the Maltese cross birefringence pattern observed in polarized light microscopy. From the peak position, the distance $d=2\pi/q_0$ between the surfactant bilayers can be calculated. We found: $d=3$ nm. This value is only slightly larger than the surfactant bilayer thickness ($\delta \approx 2.4$ nm)[37] and much smaller than the distance between the bilayers in the pure surfactant system. [For the surfactant concentration employed here, we indeed expect the spacing between the bilayers in the multilamellar vesicles to be equal to the maximum swelling of the lamellar phase, that is of the order of 80 nm.[37] Note that, with the X-ray set-up we used, the smallest wavevector available is about $0.2\ \mathrm{nm}^{-1}$; therefore one can not measure the Bragg peaks from swollen phases with periodicities larger than 32 nm, which is why we only discuss the collapsed structure of the complexes.] It indicates that the polyelectrolyte molecules induce the formation of a condensed lamellar phase. The polyelectrolyte molecules bridge the two surfactant bilayers due to the strong electrostatic attractive interaction between the headgroup of the surfactant

molecules and the charged backbone of the polyelectrolyte and are therefore confined between the surfactant bilayers of a condensed lamellar phase.[29,38,39] The condensed lamellar phase is the structure found in all cases, irrespective of the charge ratio and of the sample preparation procedure. In the samples prepared with the mixing procedure, however, an additional peak is found, when the polyelectrolyte is in excess ($x>1$), at $q^*\approx 2.44\ nm^{-1}$, corresponding to a characteristic distance $2\pi/q^*\approx 2.5$ nm. Its occurrence can be attributed to an in-plane order of the polyelectrolyte in the thin water layer between the bilayers.[27] Such in-plane order has been detected with scattering techniques for a rigid biopolymer like DNA,[29] but also by transmission electron microscopy measurements for a flexible polyelectrolyte.[40] In this reference, the texture observed within the bilayers has been attributed to the adsorbed polyelectrolyte that forms a strongly correlated two-dimensional liquid between the lipids bilayers, with a characteristic size of the order of the mesh size of the polyelectrolyte. A simple evaluation of the mesh size can be done in our case. We assume that the polyelectrolyte/surfactant complexes are neutral; hence the charges of the surfactant molecules exactly compensate those of the polyelectrolyte molecules. Each polyelectrolyte monomer occupies therefore a volume $(d-\delta)A_0=0.41\ nm^3$, in which $d-\delta=0.6$ nm is the water thickness between the surfactant bilayers and $A_0=0.68\ nm^2$[37] is the area per headgroup of the DDAB molecule. The polyelectrolyte concentration between the surfactant bilayers is therefore about 4.0 M. The mesh size (ξ) for the polyelectrolyte that we used in these investigations was measured by E. di Cola et al.[41] as a function of its concentration. Extrapolating their results to a concentration of 4.0 M gives ξ of the order of 1.5 nm. This value is in accordance with the characteristic size of 2.5 nm evaluated from the peak position, supports our interpretation of in-plane order, and in turn is a strong indication of the presence of polyelectrolyte molecules in between the surfactant bilayers.

Comments on the samples obtained by means of the "mixing" and "diffusion" procedures: From the above X-ray and light microscopy investigations, we know that the preparation procedure has a significant effect on the morphology and microstructure of surfactant/polyelectrolyte complexes. In particular, spherical, monodisperse and stable complexes can be formed, using a "diffusion" procedure. We have seen that the microscopic structure, probed by X-ray scattering, and the mesoscopic morphology, determined by light microscopy, of the complexes thus formed do not depend on the charge ratio of the surfactant/polyelectrolyte mixtures. By contrast, both the structure and the morphology of the complexes formed by simply mixing a surfactant solution and a polyelectrolyte solution depend on the charge ratio. In excess of polyelectrolyte ($x>1$), some complexes are very large and have irregular shape, which suggests that they are neutral and aggregate together. For these complexes, an in-plane order of the polyelectrolyte molecules that are intercalated between the surfactant bilayers is detected by X-ray scattering. When a "diffusion" sample ($x=3$) that has reached equilibrium is mixed, the complexes recover the features for the "mixed" sample at $x>1$, that is an in-plane order, measured by SAXS, and a morphology analogous to that of mixed samples (Figure 1c) as they interact with the excess of polyelectrolyte present in the lower surfactant solution.

Because of the stability of the spherical complexes formed using the diffusion procedure in pure water, but also in presence of positive species, and their destabilization in presence of high salt concentration or of negative species, the complexes are presumably positively charged. Hence, the "diffusion" sample preparation, whatever the relative amount of surfactant and polyelectrolyte, result in the formation of surfactant/polyelectrolyte complexes with a local charge ratio always smaller than 1. The excess of polyelectrolyte, when $x>1$, is excluded from the complexes and remains in the solution at the bottom of the vial. This view is also consistent with our observations that the complexes are destabilized upon mixing the whole "diffusion" vial.

To conclude, the striking result of our investigations is that the "diffusion" sample preparation allows one to generate surfactant/polyelectrolyte complexes that select spontaneously a given charge ratio, independently on the initial relative amount of surfactant and polyelectrolyte.

Mechanism for the formation of spherical, monodisperse complexes using the "diffusion" preparation procedure: To gain insight on the mechanisms that lead to the monodisperse spherical complexes obtained with the "diffusion" preparation procedure, we prepared a "diffusion" sample in a capillary of rectangular cross-section. With this type of chamber, one can directly access the real-time information on the complexes formation with light microscopy. We fixed one position at which initially only pure surfactant multilamellar vesicles exist. The time-evolution of the sample as the polyelectrolyte molecules diffuse toward this given position is shown in Figure 4. As observed in Figure 4a, the polyelectrolyte molecules induce first a peeling (i.e. a suc-

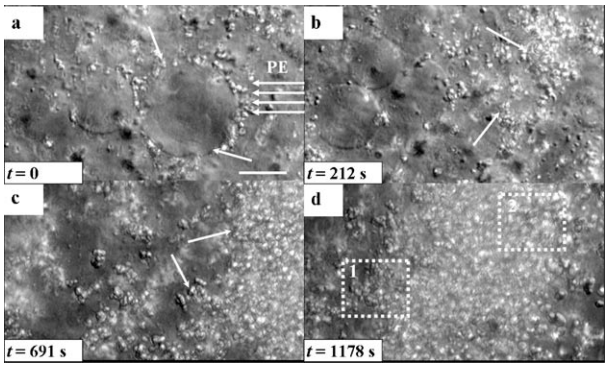

Figure 4. Micrographs showing the formation course of spherical, monodisperse polyelectrolyte/surfactant complexes. The polyelectrolyte molecules diffuse horizontally from the right to the left. The scale bar represents 20 μm. The scale is the same for the four pictures.

cessive removal of the different bilayers, starting from the most external one) of the large multilamellar vesicles and small complexes are formed around the vesicle (see the arrow in Figure 4a). We have shown previously[27] that the origin of the peeling is that the polyelectrolyte induces the formation of a pore in the external bilayer, which grows in size until complete failure of the bilayers. The freshly formed complexes that directly originate from the peeling mechanism are small, ill-defined, and polydisperse. With time, however, one observes that the size of the complexes increases and they become more spherical in shape (see the arrows in Figure 4b and c). This is presumably due to their slow and gradual growth, layer by layer, because of the continuous supply of polyelectrolyte molecules (that diffuse) and the surfactant molecules provided by the pure vesicles present in solution.

The growth of the complexes can also be clearly seen from the size difference of the complexes in two distinct regions in Figure 4d. The complexes in these two regions can be approximately considered as the complexes at different times. The complexes in region 1 correspond to the freshly formed complexes, while those in region 2, which are closer to the polyelectrolyte region, correspond to the same complexes after some time. We found that the complexes in region 1 (diameter about 2.7 ± 0.5 μm) are smaller than those in region 2 (diameter about 5.6 ± 0.6 μm).

Once the DDAB molecules are used up, the size of the complexes is expected to reach its maximum value. Then while polyelectrolyte molecules diffuse, the size of the complexes starts to decrease. This reflects the fact that, in a large excess of polyelectrolyte (x much larger than 1), no complexes are formed, and one expects the surfactant molecules to adsorb, individually or as small clusters, on the polyelectrolyte backbone.

The size decrease of the complexes in excess of polyelectrolyte can be further checked by observing the complexes at the interface between a DDAB solution and a polyelectrolyte solution (Figure 5a). The two regions highlighted in Figure 5a show the size evolution of the complexes with excess polyelectrolyte molecules around the complexes. The size of the complexes in the region 2 is about 2.4 ± 0.4 μm, which is smaller than that for the complexes in the region 1 (diameter about 5.1 ± 0.6 μm). Hence it means that the size of the complexes decreases when the surfactant molecules are used up; this result is the opposite of the kinetics of the complexes when both surfactant and polyelectrolyte molecules surround them, and when a growth of the complexes is observed. To further prove this, we show in Figure 5b complexes put in contact with a polyelectrolyte solution (1% w/w). We clearly observe that the complexes in the vicinity of the polyelectrolyte solution are smaller than they were initially. This size difference of the complexes at the interface further supports the size decrease of complexes with excess polyelectrolyte molecules, in agreement with our observation of the "diffusion" sample (Figure 5a).

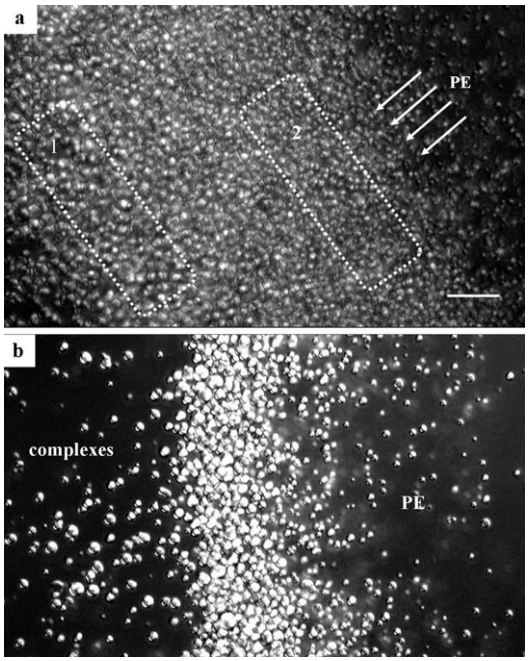

Figure 5. The complexes at the interface between DDAB and polyelectrolyte solutions in a "diffusion" preparation procedure (a) and interface between the complexes formed by means of the "diffusion" preparation procedure and a polyelectrolyte solution (b). The scale bar represents 20 μm in both a and b.

Conclusion

In summary, we have investigated complexes formed by a cationic surfactant and an anionic polyelectrolyte with different preparation procedures. In all cases, the polyelectrolyte induces a structural transition of the charged multilamellar vesicle into highly condensed lamellar complexes, presumably by bridging the surfactant bilayers, due to electrostatic attractions between the polyelectrolyte backbone and the surfactant charge headgroups. We have found that the sample preparation procedures have a major effect on the morphology and structure of the surfactant/polyelectrolyte complexes. Complexes obtained by simply mixing a surfactant solution and a polyelectrolyte solution (the "mixing" procedure) are irregular and polydisperse, while those obtained by allowing the two solutions to slowly interdiffuse (the "diffusion" procedure) are spherical and relatively uniform in size. These latter complexes are very stable when diluted in pure water or in a solution of cationic surfactants. Their high stability renders them attractive for potential application in controlled drug release. The charge ratio between the polyelectrolyte and the surfactant is a key parameter for the morphology and microscopic structure of the complexes formed in the "mixing" procedure. In marked contrast, it does not have any effect on the spherical complexes formed in the "diffusion" procedure, which are found to spontaneously select a given local charge ratio, independently of the global charge ratio of the mixtures. Observation of the samples in the time course of the formation of

the complexes by using a "diffusion" procedure suggests a slow and gradual growth of the complexes, which is presumably a key parameter for regular and uniform complexes.

Very generally, we expect the crucial role of the sample preparation procedure in the microscopic structure and mesoscopic morphology of polyelectrolyte/surfactant complexes to be universal.

Experimental Section

Materials: We used didodecyldimethyl ammonium bromide (DDAB, $(C_{12}H_{25})_2N^+(CH_3)_2Br^-$) as cationic surfactant and an alternating copolymer of styrene and maleic acid in its sodium salt form ($-CH_2CH(C_6H_5)CH(CO_2^-Na^+)CH(CO_2^-Na^+)$) as anionic polyelectrolyte. The polyelectrolyte and surfactant were purchased from Aldrich and used as received. The molar weight of the polyelectrolyte is 120000 g mol^{-1}, which corresponds on average to 454 monomers per molecule. The initial surfactant concentration was fixed at either 0.14% or 1% in weight, and its final concentration in the sample was in the range of 0.10–1% in weight, which is larger than the critical micelle concentration of DDAB[42] and lower than the concentration above which a homogeneous lamellar phase is obtained.[37] In the range of concentration used, multilamellar vesicles were spontaneously formed in solution.[37] We define x as the ratio of the number of negative charge over the number of positive charge; in our experiments, x was varied between 1/3 and 3. The polyelectrolyte concentration in the text refers to the initial added concentration and the final concentration of polyelectrolyte in the mixtures varies therefore between 0.01% and 1% in weight.

Sample preparation: The samples were prepared in two different ways. First, the polyelectrolyte solution was put in a vial, and then a suitable amount of surfactant solution, which was less dense than the polyelectrolyte solution, was gently incorporated above the polyelectrolyte solution. A sharp interface was instantly formed between the surfactant and polyelectrolyte solutions (shown in Figure 6a). It revealed the instantaneously formation of micrometric polyelectrolyte/surfactant complexes. By immediately shaking the vial shown in Figure 6a, a so-called "mixed" sample was formed (see Figure 6e). This kind of sample was turbid, indicating the presence of micrometric size polyelectrolyte/surfactant complexes in solution, and did not evolve significantly with time. In order to prepare so-called "diffusion" samples, the vial shown in Figure 6a was kept undisturbed. As time went on, the white interface gradually increased (as shown in Figure 6b–d). We defined the equilibration time as the time from which the position of the interface did not show any further change. After equilibrium, the complexes were concentrated in a thin layer at the top of the vial (see Figure 6d). They were removed with a pipette and subsequently characterized by light microscopy and X-ray scattering.

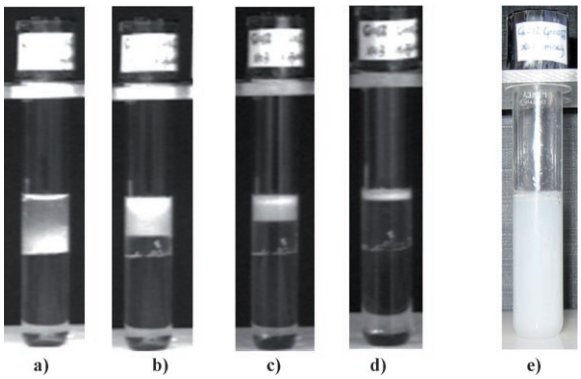

Figure 6. a)–d) Time-evolution of so called "diffusion" sample: the delay after sample preparation is a) 0, b) 2, c) 6, and d) 15 days. e) "Mixed sample". The concentration for the "mixed" and the "diffusion" samples is the same. In both cases, the initial added surfactant and polyelectrolyte concentrations are 1% and 0.5% (w/w), respectively, and the final surfactant and polyelectrolyte concentrations are 0.37% and 0.32%, respectively; the charge ratio is $x=3$.

To study the formation mechanism of the spherical monodisperse complexes in the "diffusion" sample, an analogous procedure was used in a glass capillary of rectangular cross-section 4×0.4 mm^2 (Vitro Dynamics Inc. USA, Cat. #2540), which allowed us to directly follow the time evolution of the sample by light microscopy. First the surfactant solution was placed into the capillary, then the suitable amount of polyelectrolyte solution was injected into the capillary with a micropipette.

Light microscopy observations: The surfactant/polyelectrolyte complexes formed were incorporated in a chamber made of glass slide and coverslip. Their morphology was observed with a microscope (DMIRB, Leica, Germany) by using either differential interference contrast (DIC) or crossed polarizers.

X-ray scattering experiments: Small-angle X-ray scattering (SAXS) experiments were performed by using an in-house setup with a rotating anode X-ray generator equipped with two parabolic mirrors giving a highly parallel beam of monochromatic $Cu_{K\alpha}$ radiation (wavelength $\lambda=$ 0.15418 nm). The SAXS intensity was collected with a two-dimensional detector. The distance between the sample and the detector was fixed at 313 mm. The experimental data were corrected for the background scattering and the sample transmission.

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