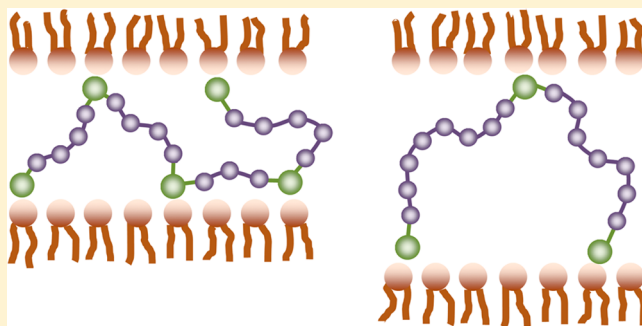


Copolymer–Surfactant Complexes Obtained in a Lamellar Lyotropic Medium

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ABSTRACT: Polymer–surfactant complexes formed between charged copolymers and oppositely charged surfactants are analyzed as a function of the charge density in the macromolecule. Copolymers of ionizable diallyldimethylammonium chloride (DADMAC) and neutral acrylamide are obtained at different comonomer ratios. When mixed with the lamellar medium formed by the anionic surfactant 1,4-bis(2-ethylhexyl)sodium sulfosuccinate (AOT) in water, they give rise to highly condensed lamellar phases in equilibrium with another lyotropic phase. The structure of these phases is studied by SAXS and optical microscopy revealing the formation of copolymer–surfactant complexes which present a lamellar structure. The composition of the phases is inaccessible to direct determination, because they do not separate macroscopically (in most of the samples). Thus, the stoichiometry is determined using a model which considers the charge density of the copolymers. This model allows, from the experimental data provided by SAXS, to calculate the composition and volume ratio of the phases. The results indicate that these complexes are nonstoichiometric, containing a lesser amount of DADMAC than surfactant units. The neutral sequences of acrylamide can be considered as bridges along the water domains remaining anchored to the AOT bilayers by the cationic DADMAC units. When the charge density diminishes, the bridges become longer, rendering structures with higher water content.



1. INTRODUCTION

Complexes involving oppositely charged polyelectrolytes and surfactants (PSCs) have constituted a very attractive field of research in the past years, owing to its importance in fundamental polymer physics, biology, and industrial applications.^{1–3} Solid-state PSCs are proposed as a new class of materials with interesting electrical, optical, and mechanical properties,⁴ while water-equilibrated PSCs have been intensively studied to improving the knowledge about biological self-assembly.⁵ It is well-known, for instance, that the interactions between phospholipid bilayers and proteins play an important role in biomembranes.⁶ Additionally, PSCs with high water content enhance the diffusion of water-soluble molecules, having potential applications in drug delivery.⁷

As a result of the electrostatic interactions between the oppositely charged units, and the hydrophobic interactions between polymer backbones and the alkyl chains of the surfactant, these systems self-assemble giving rise to the formation of diverse ordered nanostructures (i.e., lamellar,^{8,9} cubic,¹⁰ or hexagonal¹¹). The coupling of electrostatic and hydrophobic interactions is very important in determining the formation of ordered structures.¹² Therefore, their characteristics can be tuned by a large number of parameters, including global composition,¹³ length of the surfactant alkyl chain,¹⁴ length of the polymer chain,¹³ or the presence of cosurfactants.¹⁵ More precisely, the electrostatic interactions can be modulated through the macromolecular charge density^{16,17} and the ionic strength.^{18,19} These are factors that

strongly govern the complex formation, and are the ones that will be investigated in this work.

In copolymers formed by charged and neutral monomeric units, the charge density is an important parameter that modulates the interaction with the surfactant. When the charge density is low, the charges are distant along the chain, and therefore the complexes with a 1:1 stoichiometry will have a very low density of hydrophobic tails, preventing the formation of ordered structures. Such structures are favored thermodynamically only when the surfactant concentration is high enough, such that more surfactant molecules can take part in the PSC. In this case, the binding of surfactant molecules to the polymer is driven by the hydrophobic interaction,²⁰ leading to complexes with surfactant-rich stoichiometries.²¹

The dependence of the PSC structure on the charge density has been previously reported by Chu et al., who observed that the spacing of the ordered structures decreases proportionally with increasing charge density of the polymer.²²

Another important parameter in the formation of polymer surfactant complexes is the ionic strength. It is well-known that the addition of salt screens the electrostatic interaction between the surfactant and the polyelectrolyte, promoting changes in both the structure and the stoichiometry of the PSCs.²³

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Table 1. Molar Fraction of DADMAC in the Comonomer Feeding Mixture (F_D) and Data for Copolymer Characterization^a

copolymer	F_D	f_D	AAA (%)	DAA+AAD (%)	DAD (%)	$[\eta]$ dL/g	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	r
C1	0.05	0.021	99	1	-	7.8	16	6.1	2.0
C2	0.77	0.36	59	34	7	4.1	9.6	3.9	2.9
C3	0.86	0.45	44	45	11	3.1	5.1	2.3	3.3
C4	0.92	0.51	30	50	20	2.3	2.8	1.4	3.9
C5	0.98	0.68	2	57	41	2.3	2.7	0.29	5.2

^aMolar Fraction of DADMAC in the Copolymer (f_D), triads in the copolymer chains (AAA, DAA+AAD, DAD). Intrinsic viscosity ($[\eta]$), viscosity average molecular weight (\bar{M}_v), molecular weight (\bar{M}_n), and polydispersity (r).

The anionic surfactant AOT forms, in water, lamellar mesophases in a wide range of compositions. The incorporation of noninteracting neutral polymers in this system is determined mainly by entropic factors, related to the size of the macromolecule relative to the lamellar spacing, as was shown by our group in the past.^{24,25} More recently,²⁶ we have reported that the incorporation of the cationic homopolymer polydiallyldimethylammonium chloride (PDADMAC) in the lamellar AOT/water system promotes the coexistence of two lamellar phases in equilibrium that do not separate macroscopically. One of them is a collapsed lamellar phase which is a nonswollen structure with a constant lamellar spacing independent of the global water content, in which the polymer is adsorbed flat onto the bilayers forming the complex.^{27,28} The other is a swollen lamellar phase showing the typical swelling behavior (the lamellar spacing increases with the water content).^{29,30}

In this paper, we extend the study of such complexes to the case of random copolymers of cationic DADMAC and neutral acrylamide with different compositions, i.e., with several charge densities. The acrylamide units are hydrophilic and not interacting with the AOT, while the cationic units of DADMAC interact strongly with the anionic surfactant. We focus on the dependence of the structural parameters and the complex stoichiometry on the copolymer composition. The stoichiometry cannot be determined directly, because the phases formed when the polymer and the surfactant are mixed do not separate macroscopically, and hence, compositions are not accessible to direct experimental determination. This problem has been solved by developing a model which allows calculation of the composition of the phases and the stoichiometry of the complexes from the structural data of the phases. The model was previously proposed for homopolymers with fixed charge, and we extend it now to the case of copolymers of variable charge density.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The surfactant 1,4-bis(2-ethylhexyl)sodium sulfosuccinate (AOT) and acrylamide (A), both with 99% purity, were purchased from Sigma. Diallyldimethylammonium chloride (DADMAC) was provided from Aldrich as a 65 wt % aqueous solution, and 2,2'-azo-bis(2-methylpropionamide)-dihydrochloride (V-50) from Wako Chemicals. Deionized water (Milli-Q) was used throughout. AOT and DADMAC were freeze-dried before used.

2.2. Polymerization. Copolymers of acrylamide and diallyldimethylammonium chloride were synthesized in water solution at 50 °C by free radical polymerization using V50 as the initiator. The total comonomer and initiator concentrations in the feeding mixture were 3 M and 10^{-3} M, respectively. After purging with argon for 20–30 min and controlling the temperature in a water bath, the polymerization was initiated.

For the copolymer C1, with a low DADMAC content, the polymerization was performed with a conventional batch polymerization for 24 h. The other copolymers, with higher charge densities (C2, C3, C4, and C5), were obtained by seeded polymerization with dosage of the acrylamide, following the method proposed by Brand et al.³¹ Then, the copolymers C1, C2, and C3 were purified by precipitation in ethanol three times. Copolymers C4 and C5 were dialyzed with Spectra/Por membranes having 10 000 D as molecular mass cutoff. The purified polymers were dissolved in water and freeze-dried before used.

2.3. Polymer Characterization. The composition of the copolymers has been determined from the ¹H NMR spectra. The relative proportion of the triads DAD, AAA, and DAA (with its mirror image AAD) in the copolymers (Table 1) has been determined from the carbonyl resonance signal of the ¹³C NMR spectra according with the method proposed by Brand et al.³¹ The NMR spectra were obtained with a 400 MHz Bruker Avance DRY spectrometer at 27 °C using D₂O as solvent. ¹³C NMR were obtained with ¹H broad-band decoupling, and dimethylsulfoxide was used as external reference.

The intrinsic viscosity of the polymers was measured with a Lauda Viscometer in NaCl water solutions at 30 °C. The salt concentration was 0.01 M for C1 and 0.5 M for the other copolymers. These solutions were dialyzed against a salt solution with the same concentration. With this purpose, the polymer solutions were enclosed in dialysis membranes (Spectra/Por) having 10 000 D as molecular mass cutoff and contacted with an excess volume salt solution. In all cases, the outer dialysis solutions were also used as solvent in subsequent dilution procedures. The intrinsic viscosity was determined by Huggins and Kraemer extrapolations. The viscosity average molecular weight was calculated by using Mark–Houwink equations, with the exponent $a = 0.8$, and the constant $K = 6.31 \times 10^{-4}$ dL/g for copolymer C1³² and $a = 0.47$ and $K = 6.38 \times 10^{-2}$ dL/g for the other copolymers.³¹ Table 1 summarizes the data corresponding to the characterization of the polymers.

The molecular weight distributions were determined by SEC, using equipment which consisted of HP 1100 pump, an injector rheodyne of 20 μ L, a Waters 2414 differential refractive index detector, and three Ultrahydrogel columns (250, 1000, and 2000). The measurements were performed at 30 °C using aqueous 0.5 M NaCl solution as eluent and a flow rate of 0.5 mL/min. A universal calibration with 11 POE narrow standards from Polymer Laboratories (molecular weights ranging from 1.8×10^4 to 1.7×10^6) was employed. The Mark–Houwink equation for the standards was experimentally determined, obtaining $a = 0.72$ and $K = 2.25 \times 10^{-4}$ dL/g.

2.4. Sample Preparation. Two set of samples were prepared with the five copolymers, named sets C_s-# and S_c-#. Sets C_s-# are formed by six samples having the same polymer composition (1.25 wt %) and a surfactant weight fraction (#)

that varies ($\# = 20, 25, 30, 35, 40$, and 45 wt %). Sets $S_{C-}\#$ are formed by seven samples having the same surfactant composition (25 wt %) and a variable copolymer weight fraction; in the case of the C1 by nine samples ($\# = 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2$, and 3 wt %), and for the other copolymers by seven samples ($\# = 0.5, 0.75, 1.25, 2, 3, 4$, and 5 wt %). Therefore, there is one sample belonging to both sets ($C_{S-25} \equiv S_{C-1.25}$). The final composition of each sample was reached by weighing the proper amounts of AOT, polymer, and water. Samples were homogenized mixing back and forth for several days. After this process, they were allowed to equilibrate at 25°C . Additionally, six samples of the binary system AOT/water were prepared with the same surfactant concentration as the set $C_S-\#$.

2.5. Techniques for Sample Characterization. Microscopy. A microscope (Nikon Labophot-2) provided with a Nikon camera (model DS-5M) and crossed polarizers was employed to determine the anisotropy of the samples. During these measurements, the samples were placed between a glass slide and a coverslip.

Small Angle X-ray Scattering (SAXS). The experiments were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble on the beamline BM16. The samples were irradiated with a wavelength $\lambda = 0.979 \text{ \AA}$, and two-dimensional images were recorded using a CCD detector (MARCCD 165) with a resolution of 1024×1024 pixels, and a pixel size of $159 \mu\text{m}$. The sample–detector distance was 1381 mm . The images were integrated to obtain the scattered intensity (I) as a function of the modulus of the scattering vector, $q = (4\pi/\lambda) \sin \theta$, where 2θ is the scattering angle, and were normalized to compensate for the intensity fluctuations of the synchrotron source. Samples were introduced in capillaries and measured in three different locations.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization. The mixtures corresponding to the sets $C_S-\#$ are gel-like and macroscopically monophasic. The samples $C_{1S}-\#$ are turbid, while the samples $C_{2S}-\#$ and $C_{3S}-\#$ are also turbid when the surfactant concentration is lower than 30 wt % and 25 wt %, respectively. The other samples of the series $C_S-\#$ are white. The turbidity or the opacity found in the samples could indicate the coexistence of at least two phases that do not separate macroscopically.

Regarding the samples where the polymer concentration varies, all the samples from the set $S_{C1}-\#$ are gel-like, turbid, and macroscopically monophasic, while the mixtures with the other copolymers show different behavior which is depicted in Figure 1 for the set $S_{C3}-\#$ as an example. The samples with the lowest polymer concentrations are also gel-like and turbid, and become white when the polymer content increases. This transition occurs at concentrations: $2, 1.25$, and 0.75 wt % for copolymers C2, C3, and C4, respectively, i.e., when the charge density increases the transition occurs at lower polymer content. In fact, for the set $S_{C5}-\#$ this transition is not detected and the samples with the lowest polymer content are white. The turbidity or opacity of these samples suggests that the presence of polymer promotes the appearance of a new phase. In fact, when the polymer content is higher than 3 wt %, a macroscopic phase separation is observed, with the upper phase being a transparent liquid and the bottom phase a white precipitate.

Additionally, the samples have been observed between crossed polarizers. The turbid mixtures exhibit optical

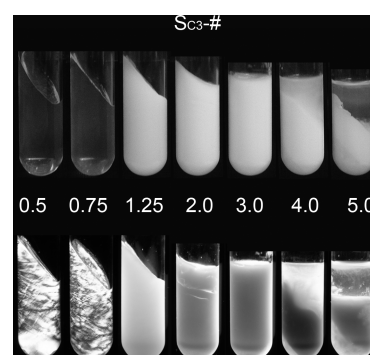


Figure 1. Pictures of the samples corresponding to the set $S_{C3}-\#$: up with and down without crossed polarizers.

anisotropy; however, in the white ones it is not detected due to their opacity (Figure 1). For the samples S_{C-4} and S_{C-5} , in which the macroscopic phase separation occurs, it is observed that the upper phase is isotropic.

The optical microscopy shows a phase separation pattern for the opaque white samples, while in the turbid samples, it is not detected. As an example, Figure 2 depicts the texture for the samples with 3 wt % of polymer content. In the micrographs corresponding to the sets of samples $S_{C-}\#$, the phase separation pattern becomes clearer as the polymer concentration increases. With crossed polarizers, the characteristic texture of a lamellar phase is detected for the turbid samples, but it is not possible to characterize the texture of the opaque white samples, due to the disturbance produced by the phase separation.

The structural order of the samples studied in this work has been determined from SAXS measurements. The binary system AOT/water, in the concentration range studied here, presents a lamellar order. Their characteristic diffraction pattern is formed by several peaks with a relative position $1:2:3\cdots$. The long period of this lamellar phase can be calculated from the first-order diffraction peak as $d = 2\pi/q$. The peak positions move to higher q values upon increasing the surfactant content. Therefore, the lamellar spacing in this swollen phase, L , decreases with the increase of the AOT content, following a dilution law³³ that can be expressed as $d = d_{\text{AOT}}/\Phi_{\text{AOT}}$ where d_{AOT} is the bilayer thickness and Φ_{AOT} the AOT volume fraction.

Additionally there are two characteristics of the AOT/water system: (i) a broad hump for wave vectors, q , between 1 and 5 nm^{-1} ,³³ which is irrespective of dilution and has been ascribed to a “strongly enhanced thermal diffuse scattering”;³⁴ (ii) the height of the first-order diffraction peak varies with the AOT concentration; first diminishes and even vanishes at $\Phi_{\text{AOT}} = 0.38$, but at higher surfactant concentration it reappears and its intensity increases. This anomalous behavior was explained in terms of a modulation by the layer displacement fluctuations.³⁴ These features were also found in the presence of a third component, e.g., decane,³⁵ or polymers²⁵ and are observed in the samples studied here. As an example, the diffractograms corresponding to the set $C_{5S}-\#$ are depicted in Figure 3a. The broad band and the extinction of the first diffraction peak of the phase L, which in this case occurs for the sample $C_{5S}-40$, are observed. This figure also shows that the presence of copolymer modifies this pattern due to the interaction of the DADMAC units with the surfactant, which induces the formation of a new lamellar phase, C. As a consequence of this phase separation, the positions and the intensities of the peaks associated with the

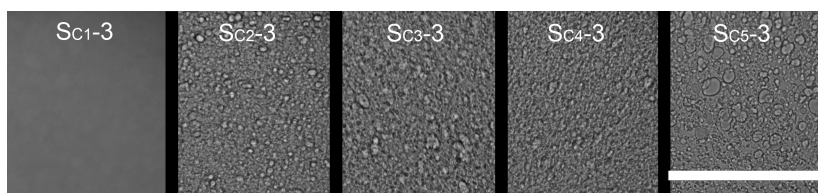


Figure 2. Micrographs without crossed polarizers of the samples with a 3 wt % of polymer content (Bar = 100 μm).

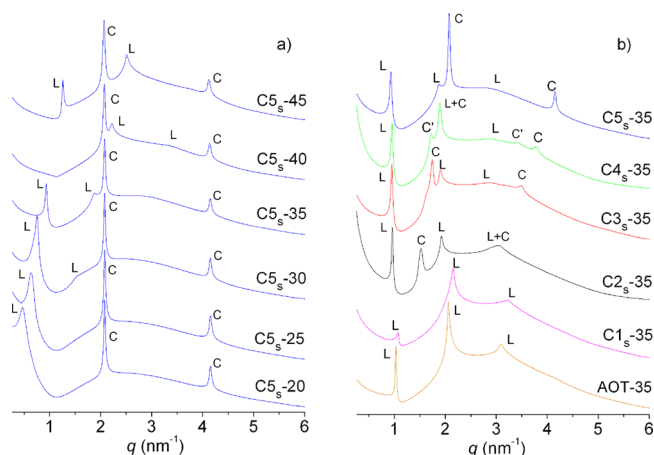


Figure 3. SAXS diffractograms corresponding to the following: a: Samples with 1.25 wt % of copolymer C5 and variable surfactant content. b: Samples with the same composition (35 wt % AOT and 1.25 wt % polymer) for the five copolymers and for the binary AOT/water system. The diffractograms have been shifted for better visualization. Intensity in arbitrary units represented in a logarithmic scale.

swollen phase are different than the expected ones in the absence of polymer, and depend not only on the composition of the samples, but also on the DADMAC content in the copolymers.

This effect can be better analyzed with Figure 3b, which compares the SAXS diffractograms of a sample with the same composition for the different copolymers. For the copolymer C1, a shift of the peaks to higher q values is observed, compared with the AOT/water binary system. This copolymer has very low DADMAC content, and therefore can be considered a noninteracting polymer. In this case, when the polymer size is high enough, the presence of polymer induces a microscopic phase separation into a polymer-rich isotropic phase (I) and a surfactant-rich lamellar phase (L). Therefore, the polymer reduces the repeat distance of the lamellar phase by osmotic compression.²⁵

For the other copolymers, additional peaks appear, also with relative positions 1:2:3... indicating the coexistence of another lamellar phase, (C). In this phase, the position of the first diffraction peak diminishes slightly with the surfactant content (Figure 3a), which can be associated with the formation of collapsed structures between ionic surfactants and oppositely charged polyelectrolytes.³⁶ It can be observed that the position of the peaks corresponding to the collapsed phase C shifts to higher q values when the DADMAC content increases (Figure 3b).

Additionally, in some samples of the copolymers C3 and C4, the presence of another collapsed lamellar phase (C') is observed. Therefore, in these samples the coexistence of three

phases is proposed: a swollen and two collapsed lamellar phases (L+C+C').

Figure 4 (left) shows the variation of the long period, d , with the polymer content corresponding to sets S_C -#. In the swollen

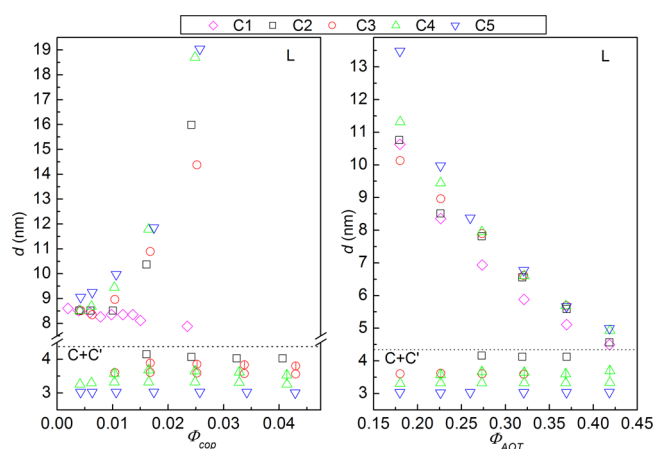


Figure 4. Lamellar spacing of the phases determined from SAXS diffractograms. Left side: as a function of Φ_{cop} for the sets S_C -#. Right side: as a function of Φ_{AOT} for the sets S_S -#. Dotted line delimits the swollen and collapsed phases.

phase, it can be observed that the long period of the samples with copolymer C1 decreases upon addition of polymer, due to the osmotic pressure exerted by the isotropic polymer-rich phase over the lamellar surfactant-rich phase.²⁵ For the other copolymers, the opposite tendency has been found, and it is observed that the addition of polymer promotes a strong swelling of this phase. This can be explained as an effect of the formation of the collapsed phase. These copolymers interact with the surfactant giving rise to the formation of a complex which generates the collapsed phases (C and C'). It is expected that the phase of the complex will contain the greatest part of the polymer^{37,38} and a fraction of the AOT and the water, while the swollen phase will be mainly composed of AOT and water. As a consequence, the surfactant content of the swollen phase decreases giving rise to the increase of d .

The variation of the long period with the surfactant is depicted in Figure 4 (right). The swollen phase follows the same tendency of the binary AOT/water system, i.e., a decrease of the long period with the surfactant content. The greater the charge density is in the copolymer, the greater the AOT incorporated into the complex. Therefore, as a general rule, the long period increases with the DADMAC content in the polymer, for a given composition.

The collapsed phase follows the same tendency in both set of samples, S_C -# and S_S -#. For each copolymer, the long period does not vary significantly with either the AOT or the polymer content. Nevertheless, a decrease of the lamellar spacing is observed as the charge density in the polymer chains increases.

The copolymer with higher charge density, C5, develops highly collapsed structures, with a lamellar spacing similar to that of the complexes of the homopolymer PDADMAC.²⁶ On the other hand, the complexes formed by the copolymers with lower charge density are more swollen, as expected due to the increase of the hydrophilic groups, i.e., their acrylamide content.

For the copolymers with intermediate charge density (C3 and C4), the formation of a new collapsed structure, C', with higher long period has been detected. To explain this result, it could be argued that these copolymers have a bimodal composition distribution, but in spite of some experimental measurements performed in order to elucidate this aspect (SEC, NMR, not shown here), it was not possible to prove it. Another possibility is that these copolymers give rise to complexes with two preferential polymer conformations. In fact, Poghosyan et al.³⁹ reported a molecular dynamics study of (PDADMAC) in sodium dodecyl sulfate/decanol/water system in which the existence of two preferential conformations is proposed, a flat conformation where the PDADMAC molecule is adsorbed at the anionic head groups of the surfactant molecules, and a more folded structure, that could correspond to the structures C and C', respectively.

3.2. The Model. In most of the samples, there are two phases (L and C) that do not macroscopically separate. The absence of macroscopic phase separation precludes direct determination of the composition of these phases. Therefore, their composition, the volume ratio of these phases, and the stoichiometry of the complexes cannot be experimentally determined, and a model should be proposed to obtain this information.

Previously, we developed a model for homopolymers (PDADMAC) in which all the monomeric units are charged.²⁶ For copolymers with variable charge density, it is necessary to modify this model with the aim of considering the composition of the polymer.

The copolymers are formed by DADMAC and acrylamide and it is expected that the DADMAC units adsorb onto the anionic head groups of AOT, due to the electrostatic interaction, while the acrylamide units do not strongly interact with the surfactant. For this reason, the acrylamide segments will locate preferentially in the water region. Therefore, the formation of complexes with a variable stoichiometry (molar ratio between the DADMAC units in the chain and the number of surfactant heads, n_D/n_{AOT}) and with variable water content as a function of the copolymer composition is expected.

The starting point of the model is to assume a given stoichiometry. From this, we calculate the thickness of the layer of the complex, i.e., the thickness of the layer formed by the DADMAC units adsorbed onto the surfactant bilayer, d^* . Afterward, with d^* and taking into account the composition of the copolymer and the experimental spacing between lamellae in the collapsed phase, we can obtain the composition of phase C (see Appendix I for a detailed explanation of this process). For the complete characterization of the samples, it is necessary to obtain the composition of the swollen phase, the volume ratio between a given phase (L or C), and the total volume, as well as an optimization process for controlling the validity of the model and the proposed stoichiometry. The corresponding expressions, previously reported for the PDADMAC,²⁶ are also valid for its copolymers and have been employed in this work. The results obtained with this model are analyzed in the following.

3.3. Composition of the Phases. In order to compare the effect of the different composition of the copolymers, Figure 5

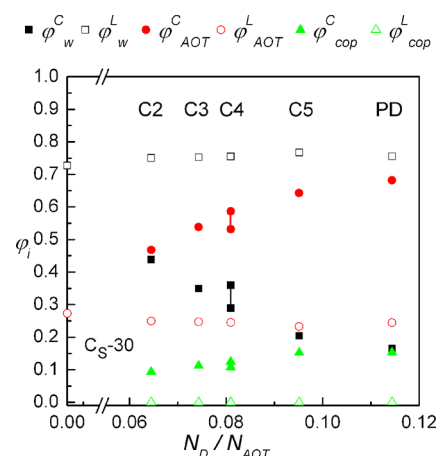


Figure 5. Composition of the swollen phase (L) and the phases of the complex (C, C') as a function of the DADMAC/AOT molar ratio of the samples (N_D/N_{AOT}), for the samples with a global composition of 30 wt % AOT and 1.25 wt % polymer. For copolymer C4, the two points depicted per component indicate the range of composition for the phases C and C'. The points corresponding to the binary AOT/water system are also included.

depicts, as an example, the composition of the phases obtained for the samples C_S-30 as a function of the DADMAC/AOT molar ratio of the samples (N_D/N_{AOT}), which can be calculated from the amount of AOT and copolymer in each sample and the composition of the copolymers. In this figure, there are also included the data corresponding to the binary AOT/water system and those of the samples with PDADMAC (PD, from ref 26). An important variation in the composition of the phase of the complex is observed when the copolymer is enriched with DADMAC; the proportion of water decreases, while the polymer and AOT increases. This could be explained by taking into account that the acrylamide units prefer to be located in a water environment, while the DADMAC units adsorb onto the AOT bilayer.

The model is only valid when two phases coexist (L and C). Therefore, in the case of the samples presenting three phases, one swollen and two collapsed (L, C, and C'), the results do not fit the model. In spite of this, a range for the composition of these phases can be obtained if the model is applied twice: first assuming the existence of the phases (L+C), and then considering (L+C'). In Figure 5, the results for the sample C_{4S}-30, which presents two collapsed phases, has been obtained following this process, and the two points depicted per each component delimit the composition range.

The concentration of polymer in the swollen phase is practically negligible and, therefore, it is composed mainly of AOT and water. Additionally, there are no significant variations in their compositions, which extrapolate to those of the binary system. This occurs because the global amount of polymer in these samples is low (1.25 wt %), and it is expected that the amount of phase C will also be low, as we will see below.

The model allows us to obtain the volume fraction of the swollen lamellar phase (V^L/V_T), which is depicted as a function of N_D/N_{AOT} in Figure 6. The data corresponding to the PDADMAC are also included. For the samples S_C-, the proportion of the swollen lamellar phase decreases with the

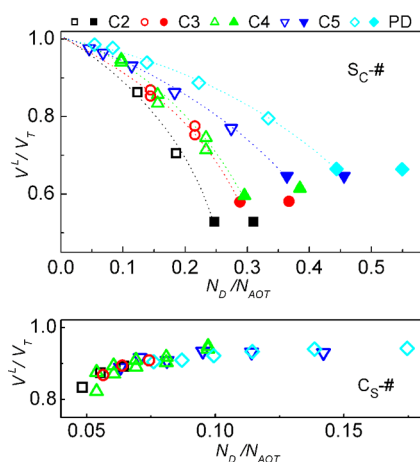


Figure 6. Volume fraction of the swollen lamellar phase (V^L/V_T) for the copolymers and PDADMAC (PD, from ref 26) as a function of N_D/N_{AOT} . Open symbols: samples without macroscopic phase separation. Closed symbols: samples with macroscopic phase separation. The lines are drawn only as guides for the eyes.

polymer content. It can also be observed that this variation becomes more important as the DADMAC content in the copolymer decreases. In other words, a greater amount of phase C is formed as the acrylamide copolymer content increases. This occurs because there is more water incorporated in the complex (see Figure 5).

When the polymer concentration is high enough, most of the AOT goes to the phase of complex and, therefore, the swollen lamellar phase disappears, becoming isotropic. For each copolymer, the trend line joining the samples without macroscopic phase separation, extrapolates to the first sample in which the swollen lamellar phase becomes isotropic (4 wt % polymer). In this isotropic phase (M), the AOT concentration is low and, therefore, the volume ratio in these samples can be calculated with the same model, but assuming that the whole AOT and polymer are in the phase of the complex.

Figure 6 shows also that in the sets of samples where the surfactant concentration varies, V^L/V_T diminishes upon increasing the global AOT concentration. In these samples the polymer content remains constant and the variation is due to a greater incorporation of AOT and water in the complex.

Although in most of the systems a detailed study of the stoichiometry has not been performed, it is usually assumed that the composition of the PSCs is stoichiometric, with equal amounts of the two species of opposite charge.^{40,41} Nevertheless, in some cases the existence of nonstoichiometric complexes has been proven.^{23,42} In our previous work, it was demonstrated that the stoichiometry of PSCs formed with PDADMAC depends on the composition of the samples, and this effect has also been found for the copolymers.

Figure 7 shows that, in the series $C_S\text{-}\#$, the lowering of the surfactant concentration produces an increase of N_D/N_{AOT} , which induces an increase of the stoichiometry of the complexes (n_D/n_{AOT}), as expected. On the other hand, in the series where the polymer concentration varies, $S_C\text{-}\#$, the stoichiometry of the complexes (n_D/n_{AOT}) diminishes upon increasing the polymer content in the samples, as occurs for PDADMAC. To explain this apparently unexpected result, it should be taken into account that, when the complex is formed, the AOT units interact with the DADMAC ones, releasing to the medium their counterions (Cl^- and Na^+). As was

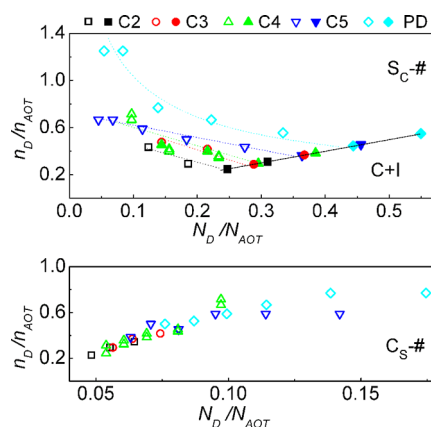


Figure 7. Stoichiometry of the polymer surfactant complexes (n_D/n_{AOT}) as a function of the DADMAC/AOT molar ratio of the samples (N_D/N_{AOT}). Open symbols: samples without macroscopic phase separation. Closed symbols: samples with macroscopic phase separation. The lines are drawn only as guides to the eyes.

previously proposed, the increase of the ionic strength induces the formation of complexes with higher surfactant content.²³ The variation of the stoichiometry could be associated to a conformational change of the polymer molecule, which can be promoted by a lowering in the effective charge density produced by the screening counterions.⁴³ This is not the case for the $C_S\text{-}\#$ series, where the stoichiometry is governed by the excess of surfactant, since the amount of salt released to the medium when the complexes are formed is very low and approximately the same.

This trend extrapolates to the point in which the swollen lamellar phase becomes isotropic (samples $S_C\text{-}4$), and from this, the trend line varies. In order to understand this, the swollen lamellar phase can be considered an AOT reservoir. Hence, as the polymer is added, the amount of AOT available to be incorporated in the complex diminishes. When the isotropic phase M appears, the AOT concentration is too low, and from this moment, it can be considered that the stoichiometry is given by the total amounts of DADMAC and AOT in the sample.

Additionally, it is observed in both series that the stoichiometry increases with the DADMAC content in the copolymers. To understand this, it should be considered that in the copolymers with lower DADMAC content there is a long distance between the charged units and, additionally, their complexes incorporate more water due to their high acrylamide content. As a consequence, a higher amount of AOT is required to form lamellar complexes, as illustrated in Scheme 1.

Figure 8 presents the phases of the samples studied here. For the copolymer with the lowest DADMAC content (C1) all the samples show the coexistence of a swollen lamellar and an isotropic polymer-rich phase (L+I), without macroscopic phase separation. For the other copolymers, the phases L+I also coexist when the surfactant and DADMAC contents are low enough. Nevertheless, when the surfactant and DADMAC contents increase (either due to the increase of the DADMAC in the copolymer or the polymer content), polymer surfactant complexes are formed, remaining in equilibrium with the swollen lamellar phase (L+C or L+C+C'). For the samples with higher polymer content (4–5 wt %), the greatest part of AOT remains with the polymer in the PSCs, promoting the formation of an isotropic micellar phase and the macroscopic

Scheme 1. Variation of the Stoichiometry as a Function of the DADMAC Content in the Copolymer

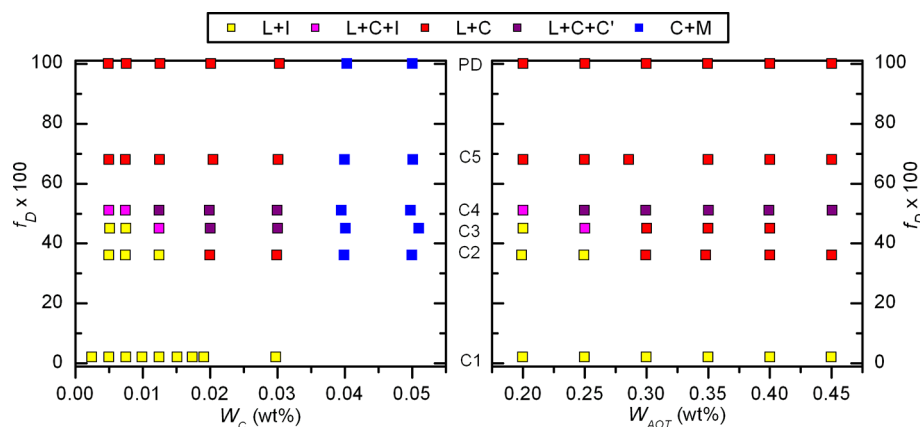
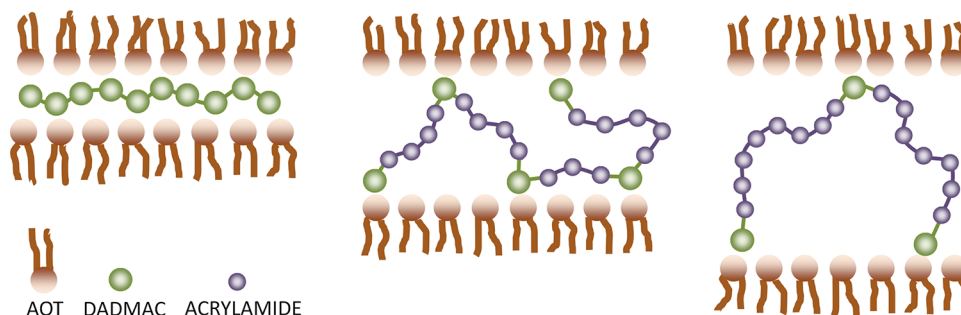


Figure 8. Phase diagram of the samples studied in this work as a function of the frequency of the cationic monomer in the copolymer (f_D) and the composition of the samples. Left: samples S_C -#, with 25 wt % AOT and variable weight polymer fraction (W_C). Right: samples C_S -#, with 1.25 wt % polymer and variable weight surfactant fraction (W_{AOT}).

phase separation (C+M). In the transition between the samples with structures L+I and those with structures L+C, there are some samples with three phases (L+C+I).

4. CONCLUSIONS

In this work we studied the effect of incorporating copolymers with variable charge densities in the AOT/water lamellar medium. The copolymers with very low charge density do not form ordered complexes, while the copolymers with high charge density render complexes with lamellar order. In the case of copolymers with intermediate charge density, there are critical concentrations of AOT and polymer to obtain complexes with ordered structure.

Since in most of the samples there is no macroscopic phase separation, the composition of the phases by experimental techniques is hindered and it is necessary to resort to a model in order to deepen its knowledge. Here, a model is proposed that takes into account the variation of the charge density of the polymers and allows the stoichiometry of the complexes and the composition of the phases to be obtained. In the model, the DADMAC units adsorb onto the anionic head groups of AOT, due to the electrostatic interactions, while the acrylamide units locate in the water region.

The stoichiometry of the complexes (n_D/n_{AOT}) depends on the composition of the samples and the copolymer charge density as follows: (i) When the surfactant or the polymer concentration increases, the complexes are enriched in AOT. (ii) The lowering of the polymer charge density induces the formation of complexes with higher AOT content and also with higher water content. The use of copolymers with variable charge density makes possible the design of complexes with

tunable water content, which could be appropriate for several applications, e.g., drug delivery.

■ APPENDIX I

A dilution law for the lamellar complex similar to that of a swollen lamellar phase can be proposed. Therefore:

$$d^C = d^* + d_{W+A}^C \quad (1)$$

where d^C is the characteristic lamellar spacing of the complex (determined experimentally), and d^* corresponds to the thickness of the D/AOT complex (disregarding the water and acrylamide). If it is assumed that the D charged units are adsorbed onto the AOT bilayers, with a characteristic thickness, d_D , then:

$$d^* = d_{AOT} + d_D \quad (2)$$

where $d_{AOT} = 1.95$ nm, obtained from the binary AOT/water system. Finally, d_{W+A}^C represents the thickness of the layer containing the water and the acrylamide segments from the copolymer.

Taking into account that this is a lamellar system, the ratio between d_D and d_{AOT} will be equivalent to the ratio between the volumes of D and AOT in the complex (V_D^C and V_{AOT}^C):

$$\frac{d_D}{d_{AOT}} = \frac{V_D^C}{V_{AOT}^C} \quad (3)$$

On the other hand, it is clear that this ratio is proportional to the molar ratios of the two charged units in the complex (n_D/n_{AOT}) and their molecular weights (M_D/M_{AOT}):

$$\frac{V_D^C}{V_{AOT}^C} = \frac{\rho_{AOT} M_D}{\rho_{PD} M_{AOT}} \frac{n_D}{n_{AOT}} \quad (4)$$

where $\rho_{AOT} = 1.14$ g/mL, and $\rho_{PD} = 1.23$ g/mL are the densities of AOT⁴⁴ and PDADMAC,²⁶ where it is assumed that the density of the DADMAC units in the copolymer is similar to the density of the homopolymer.

The volume of the phase of the complex (V^C) will be the sum of the volumes of the whole components:

$$V^C = V_D^C + V_A^C + V_{AOT}^C + V_w^C \quad (5)$$

where V_A^C is the volume corresponding to the acrylamide segments and V_w^C is the water volume. After dividing by V^C , eq 4 renders:

$$\frac{V_D^C}{V_{AOT}^C} = \frac{\phi_D^C}{\phi_{AOT}^C} \quad (6)$$

being ϕ_D^C and ϕ_{AOT}^C the volume fractions corresponding to the DADMAC and AOT units in the phase of the complex.

From eqs 2, 3, and 6, one can obtain

$$d^* = d_{AOT} \left(1 + \frac{\phi_D^C}{\phi_{AOT}^C} \right) \quad (7)$$

Once the value of d^* is known, it is possible to estimate d_{w+A}^C with eq 1, and consequently the water volume fraction in this phase, ϕ_{w+A}^C , as

$$\phi_{w+A}^C = \frac{d_{w+A}^C}{d^C} \quad (8)$$

On the other hand, the expression

$$\phi_D^C + \phi_{AOT}^C + \phi_{w+A}^C = 1 \quad (9)$$

can be transformed to give

$$\phi_{AOT}^C = \frac{1 - \phi_{w+A}^C}{1 + \frac{\phi_D^C}{\phi_{AOT}^C}} \quad (10)$$

which allows determination of ϕ_{AOT}^C and ϕ_D^C , since ϕ_{w+A}^C and ϕ_D^C/ϕ_{AOT}^C were previously calculated.

The volume fraction of DADMAC in the copolymer, α , is defined as

$$\alpha = \frac{V_D}{V_D + V_A} \quad (11)$$

where V_D and V_A correspond to the volumes of DADMAC and acrylamide in each copolymer. Therefore, it can be determined from the composition of the copolymers and the densities of the homopolymers.

Once α and ϕ_D^C are known, it is possible to obtain the volume fraction of the copolymer in the phase C, ϕ_{cop}^C

$$\phi_{cop}^C = \frac{\phi_D^C}{\alpha} \quad (12)$$

Then, the volume fraction of water in the phase of the complex ϕ_w^C can be calculated as

$$\phi_w^C = \phi_{w+A}^C - (1 - \alpha)\phi_{cop}^C \quad (13)$$

The above model allows estimation of the composition of phase C as a function of the stoichiometry and the composition of the copolymers.

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Notes

The authors declare no competing financial interest.

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