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The effect of poly(N,*N*-dimethylacrylamide) on the lamellar phase of Aerosol OT/water

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Abstract The effect of a water-soluble uncharged polymer on the stability of the lamellar phase of the Aerosol OT (AOT)/water system is studied. The lamellar phase still exists when water is replaced by an aqueous solution of poly(*N*,*N*- dimethylacrylamide) ($R_g \approx 4\times10^2$ Å). Since the coil dimensions are (much) larger than the thickness of the water layers ($d_w \approx 51$ Å), the polymer molecules do not enter the lamellar phase. Instead segregation in small domains occurs, and in equilibrium with the AOT-rich phase another separate phase containing the polymer is formed. The polymer-rich phase exerts an osmotic pressure that reduces the water content in the AOT-rich phase, and by compression the repeat distance is reduced.

Keywords Lamellar · Aerosol OT · Poly(*N*,*N*-dimethylacrylamide) · Segregation

Introduction

It is well known that macromolecules may alter properties of lyotropic mesophases of a surfactant in solution, and from a fundamental research point of view the effect of an added polymer has received interest in recent years. In particular, the influence on the lamellar phase (L_α) has been investigated since there are some industrial processes [1], as well as biomembrane processes [2], that take advantage of such polymer-induced changes. In general a lamellar phase consists of bilayers of surfactant molecules oriented tail-to-tail and separated by solvent molecules (here water), and when a polymer is added to this type of system, depending on the physical properties of the polymer and on the polymer/surfactant interactions, the polymer chains can be

1. Dissolved within the surfactant membrane [3].
2. Adsorbed onto the bilayer [4, 5].
3. In the water domains [6, 7, 8].

In the first case the bilayer thickness, d_0, changes while in the third case the addition of polymer is likely to lead to a change in the water layer thickness, d_w. The second case is intermediate and is expected to give a change in d_0 and/or the surfactant headgroup area, as well as in d_w.

Regarding case 3, addition of the polymer may either increase or decrease the thickness of the water layers. The increase occurs when the polymer chains dissolve in the water layers between the lamellae, while d_w decreases when the polymer chains are excluded from the lamellar phase and are located in a new separate phase (segregation). The behavior is determined by the free-energy difference between the monophasic system and the phase-separated system [6, 9]. However, pure geometrical considerations are often enough to envisage the location of a water-soluble polymer. Such predictions are based on the relative average dimensions of the polymer coils and the thickness of the water domains in the lamellar phase. Thus, in this view the requirement to

have single-phase behavior is that $2R_g < d_w$ (R_g is radius of gyration of the polymer coils). If this is not the case, it is obvious that polymer chains entrapped between the lamellae will only have the possibility to take on a reduced number of conformations. This situation is associated with a loss in conformational entropy of the polymer chains, and is therefore less likely. Nevertheless, this has been reported to occur in some cases [10]. This could also happen when interlamellar repulsions are strong and it is more favorable to compress the polymer coils than to reduce the water content in the lamellar phase. In passing, we note that one fundamental reason to study a system in which polymer chains are incorporated into the L_α phase is that a two-dimensional space is provided [6].

With polymer entrapped in the lamellar phase it has been suggested that interlayer interactions are changed by mechanisms such as excluded-volume effects and modification of the electrostatic interactions [11]. In fact, it has been suggested that a lamellar phase of an ionic surfactant can be destabilized as a result of a reduced repulsive electrostatic potential [4, 11]. Thus, when a nonionic polymer is incorporated in the lamellar phase of an ionic surfactant two situations may arise: If the polymer/surfactant interactions are attractive the sample may remain monophasic, while if the interactions are repulsive the sample may separate into two lamellar phases in equilibrium. One phase is surfactant-rich and has a relatively small thickness of the water layers, d_w, while the other is polymer-rich with a larger d_w. This has been extensively studied for the lamellar phase of the cetylpyridinium chloride/hexanol/water system on addition of poly(vinylpyrrolidone) [6, 7].

In the second case mentioned earlier, when the polymer chains are located outside the lamellar phase, a depletion mechanism operates and the repeat distance of the lamellar phase is reduced by osmotic compression from the polymer-rich phase.

In a study by Zhang and Linse [9] the effect of poly(ethylene oxide) in the Aerosol (AOT)/water lamellar system was investigated. They found that poly(ethylene oxide) dissolves either in the aqueous domains of the lamellar mesophase or in a separate polymer-rich isotropic phase in equilibrium with the lamellar phase. In line with the previous discussion, they concluded that the relative sizes of d_w and R_g were essential for the outcome.

This is the basis for the present work and we have focused on the effects of a large ($R_g \approx 4\times10^2$ Å) nonadsorbing, nonionic polymer, poly(*N*,*N*-dimethylacrylamide) (PDMAA) on the AOT/water lamellar mesophase, where the distance between the lamellae is comparatively small ($d_w \approx 51$ Å). In addition to phase studies and structural investigations, fluorescence measurements give us complementary information about where the polymer chains are localized.

Experimental

Materials

The AOT and *N*,*N*′-dimethylacrylamide were of 99% purity and were obtained from Sigma and Aldrich, respectively, and pyrenilmethyl methacrylate was purchased from Polyscience. These chemicals were used as received. The solvent was water of reactivity quality (Milli-Q) except for that used in the NMR studies where deuterated water (99.5% purity) purchased from Dr. Glaser, Basel, was used.

Synthesis of *N*-(2-aminoethyl)-5-(dimethylamino)naphthalene sulfonamide

N-(2-Aminoethyl)-5-(dimethylamino)naphthalene sulfonamide (S) was used as a fluorescent probe, and the synthesis procedure is described elsewhere [12, 13]. S was obtained as pale-green needles with a melting point of 139 ± 10 °C. The yield of the reaction was 30% and the structure was confirmed from NMR spectra obtained in a water/acetone mixture (50/50 by weight). The chemical shifts of S (Fig. 1) were (a) 8.58–8.54 (d), (b) 8.39–8.34 (d), (c) 8.27–8.19 (d), (d) 7.67–7.50 (m), (e) 7.29–7.25 (d), (g) 3.17–3.01 (m), (f) 2.88–2.73 and water (two s overlapped), 2.88–2.74 acetone (m) [12, 13, 14].

Synthesis and characterization of PDMAA

A solution of 8% dimethylacrylamide in water with azobis(isobutyronitrile) (initiator), previously crystallized from methanol, 10^{-3} M, was sonicated for 15 min and incubated at 62 °C for 20 h. The PDMAA synthesized was precipitated in cold acetone, and later dried at 40 °C. Its ^{1}H NMR spectrum showed no vinyl signals. The intrinsic viscosity of the polymer was determined in water at 25 °C, and Huggins and Kraemer extrapolations gave $[\eta] = 4.26$ dl/g. This value corresponds to an overlap concentration $c^* = 1/[\eta] = 2.3$ g/l. The viscosity-average molecular weight, calculated by using the Mark–Houwink equation [15] with the exponent $a = 0.81$, and the constant $K = 2.24\times10^{-5}$ dl/g, is $\overline{M_v} = 3.3 \times 10^6$ g/mol. The radius of gyration in water could be estimated as $R_g \approx 491$ Å by using $R_g^2 = C_\infty N l^2/6$. Here the characteristic ratio $C_\infty = 9.15$ was obtained from the literature [15], the number of bonds in the main chain, N, was calculated from the polymer molecular weight and l is the bond length. The size of the polymer coils in water was also estimated by self-diffusion NMR in the limit of infinite dilution of the polymer. The NMR experiment was evaluated by using a Stejskal–Tanner analysis where the spin-echo attenuation was described by a stretched exponential. The mean self-diffusion coefficient, D_m, was then transferred to a hydrodynamic radius, $R_h = 258$ Å by using the Stokes–Einstein equation, $R_h = kT/6\pi\eta D_m$. With a polymer in a θ-solvent it is frequently

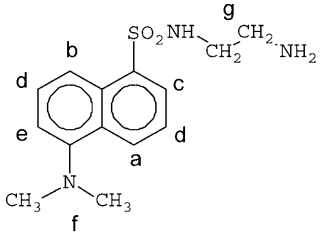

Fig. 1. The fluorescent compound *N*-(2-aminoethyl)-5-(dimethylamino)naphthalene sulfonamide (*S*) which was added as a probe in some of the samples. *a–g* identify the different hydrogen atoms detected by NMR

found that $R_g/R_h \approx 1.5$, which suggests $R_g \approx 378$ Å. In conclusion we can say that the polymer coils have a radius of gyration of about 4×10^2 Å. This will be important in the discussion later since the average interlamellar spacing, d_w, between the AOT bilayers is much smaller.

Synthesis and characterization of PDMAA-*co*-pyrenilmethyl methacrylamide

The labeled polymer PDMAA-*co*-pyrenilmethyl methacrylamide (PDMAA*) was obtained by the same procedure as the nonlabeled PDMAA but by also including 10^{-8} M pyrenilmethyl methacrylate in the feed mixture. After the reaction this compound was treated in the same way as the nonlabeled PDMAA but in addition it was also washed with diethyl ether to remove pyrenilmethyl methacrylate that had not been covalently bonded to the polymer chains. By fluorescence spectroscopy the composition of PDMAA* (with respect to pyrenilmethyl methacrylate) could be determined by using a calibration curve obtained by dissolving free pyrenilmethyl methacrylate in dioxane. The mole fraction of the fluorescence label incorporated in the copolymer was determined by this method to be 1×10^{-5}. This low concentration of the fluorescence label should ensure that the characteristics of the polymer chains are virtually the same as for the unlabeled polymer. Here it can be noted that it was not possible to employ UV–vis absorbance to determine the composition because of a too much light scattering from the final polymer solution in this wavelength range.

Sample preparation

The samples were prepared by weighing proper amounts of the different components directly into glass tubes that were then flame-sealed. The samples were homogenized by repeated centrifugation of the mixtures back and forth, and then they were left to equilibrate for 20 days at 25 °C before any measurements were conducted. Three series of samples were prepared, keeping in all cases the ratio of surfactant to water constant. One set (the P set) had an AOT/H_2O weight ratio of 0.37 ± 0.02 and a polymer concentration that was varied between 0.05 and 3.49 wt%. These samples are referred to as PX:Y, where X and Y are the amounts of AOT and of polymer, respectively, both given in weight percent. The second set (the PS set) contains the corresponding samples but with the fluorescent probe S also included. S was added at a concentration $1.63\pm0.09\times10^{-3}$ wt% in all the samples. Each sample in this set is referred to as PSX:Y, where X and Y have the same meaning as in the P set. The third set contains the samples to be used in the ^{2}H NMR measurements. To compensate for the changed molecular weight of the water, this set was prepared with an AOT/D_2O ratio corresponding to 0.34 ± 0.02 wt%. This gives the same molar ratio as in the PX:Y samples. The PDMAA concentration in this set ranged from 0 to 7.47 wt%. The samples in this set are referred to as DPX:Y.

Finally, a sample called PP25:8 containing 25 wt% AOT and 8 wt% fluorescence-labeled polymer, PDMAA*, was prepared.

Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) measurements were performed using a Kratky compact small-angle system equipped with a position-sensitive detector (OED 50M, M. Braun, Graz, Austria) containing 1,024 channels, each with a width of 53.6 μm. Cu K_α radiation of wavelength 1.54 Å was provided by a Seifert ID-300 X-ray generator, operating at 50 kV and 40 mA. A 10-μm-thick nickel filter was used to remove the K_β radiation, and a 1.5-mm tungsten filter was used to protect the detector from the primary beam. The beam width (defined as where the intensity is half that at the maximum) was 0.59 mm. The sample-to-detector distance was 277 mm. In order to minimize scattering from air and to increase the signal-to-noise ratio, the volume between the sample and the detector was under vacuum. During the measurement the samples were placed in a capillary and the temperature (25 °C) was controlled to within 0.1 °C by using a Peltier element.

^{2}H NMR

Deuterium spectra were recorded using a Bruker DMX 100 spectrometer operating at a deuterium resonance frequency of 15.35 MHz. The pulse length was 10 μs and the receiver dead time was set to 25 μs. The temperature was kept at 25 ± 0.2 °C by a flux of air through the sample holder. The samples were kept in 8-mm test tubes that had been flame-sealed. The quadrupole splittings, Δ, were measured as the peak-to-peak distance and are reported in hertz.

Steady-state fluorescence spectroscopy

Fluorescence emission spectra were recorded using an Aminco Bowman SLM 2. The emission spectra were corrected using the instrumental response at each wavelength, and for each spectrum the experimental conditions (slit width and excitation wavelength) are indicated.

Optical microscopy

A microscope (Zeiss Axiopan) provided with a Hamamatsu camera (model L2400-08) 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 cover slip.

Results and discussion

In this work the lamellar liquid-crystalline phase (L_α) of AOT/water mixtures was investigated with respect to the phase stability and the microstructure with an increasing PDMAA content. At 25 °C and without added polymer, the L_α phase extends from 20 to 70 wt% of surfactant and consists of a regular array of AOT bilayers alternated with water layers [10, 16]. The other component in our mixtures, the PDMAA polymer, is water-soluble and forms optically clear solutions. To be able to interpret our results in the correct way it is also important to know whether AOT and PDMAA associate. Since association is followed by a change in the critical concentration where surfactant molecules aggregate to form (polymer-bound) self-assembled structures such information can be obtained in the following way. The conductivity as a function of surfactant concentration (of a solution of an ionic surfactant, like AOT) has an inflection point at the stage where aggregates start to form. By comparing the concentration at this point in systems with and without polymer it is therefore possible to determine whether the surfactant aggregates bind to the polymer chains. Such conductivity curves for AOT, with and without PDMAA, are presented in Fig. 2. Since the polymer has no significant influence, we conclude that there is no experimental evidence of association. This

strongly suggests that PDMAA will only be in the water domains (like in case 3 as discussed in the Introduction) and will not be found within the surfactant membrane or adsorbed onto the AOT bilayers.

Already at this stage it deserves to be mentioned that AOT samples that contain PDMAA are sometimes turbid, and that the turbidity often increases with the polymer concentration. This could indicate that PDMAA has induced a phase separation. However, despite prolonged centrifugation, macroscopic separation into two phases could not be obtained, the reason being a combination of high viscosity and a too small difference in density (between the phases), so the kinetic phase separation should be extremely slow. In fact similar behavior has been found for other systems, i.e., poly(vinyl pyrrolidone) in a brine swollen-surfactant lamellar phase, where the phase separation was obtained after more than 2 years [6]. While macroscopic phase separation was inaccessible, the fact that neither the ^{2}H NMR or the SAXS spectra changed significantly over a 5-month period of time indicated that microscopic equilibrium had already been obtained after the initial 20 days (see Sample preparation).

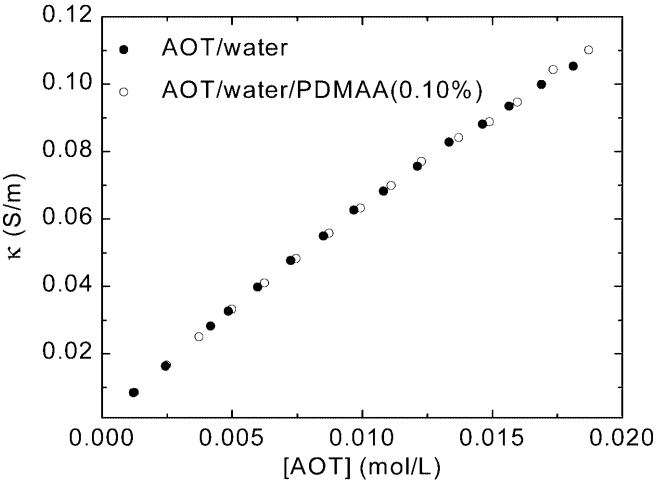

Fig. 2. Conductivity of Aerosol OT (*AOT*) water solutions without and with 0.10 wt% poly(*N*,*N*- dimethylacrylamide) (*PDMAA*), as a function of AOT concentration

Optical microscopy

Micrographs from the samples obtained with crossed polarizers show a marbled birefringent texture (Fig. 3). This texture appears in all the samples that we studied and it is typical of an L_α phase. Thus, as judged from the micrographs, addition of polymer does not seem to modify the birefringent properties. However, as mentioned earlier, increased turbidity was observed when polymer was added, which we take as an indication of a phase separation. In such cases spherulites usually appear in the textures. They are typical defects of

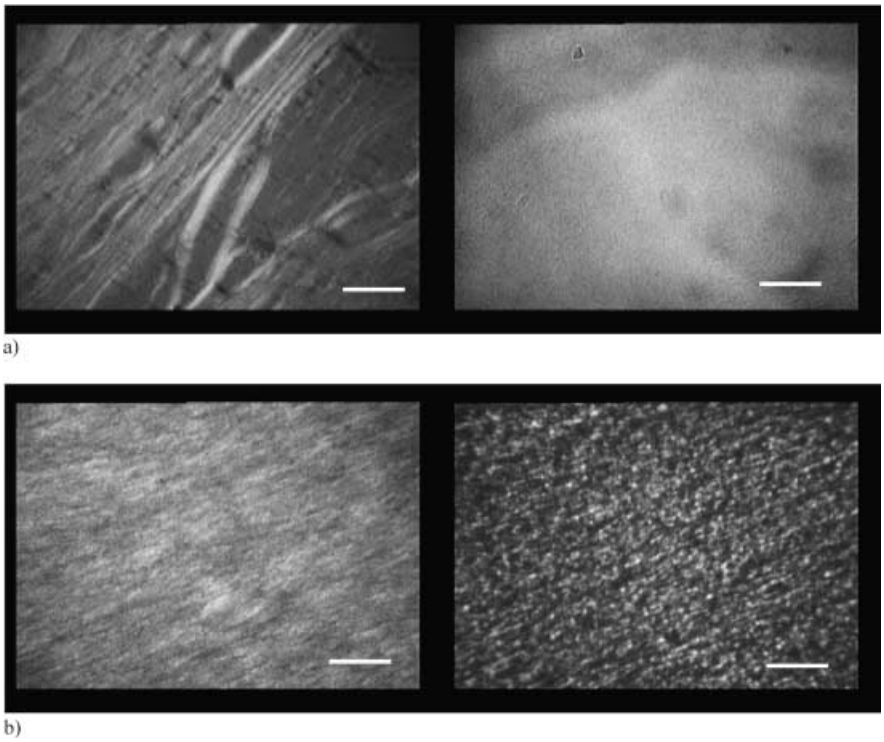

Fig. 3a,b. Two micrographs showing the marbled birefringent texture that appears in all the samples studied in this work (pictures on the *left*). The pictures on the *right* were obtained without crossed polarizers. *Bar*: 100 μm. **a** sample DP25:0.2 with 25 wt% AOT and 0.2 wt% PDMAA and **b** sample DP23:7.5 with 23 wt% AOT and 7.5 wt% PDMAA, both with D_2O as solvent

a lamellar phase dispersed in an isotropic phase [17] but we did not detect this kind of defect in the textures of our samples. Referring to the micrographs obtained without crossed polarizes (Fig. 3) they show a phase-separated pattern which becomes clearer as the polymer concentration increases. We conclude that the separate phase domains are large enough to scatter light (bigger than 10–100 nm) but are smaller than 10 μm.

Small-angle X-ray scattering

SAXS measurements provide information about the structure, and some typical diffractions patterns for the samples in this investigation are presented in Fig. 4 (the P*X*:*Y* series is shown), revealing the features expected for the L_α phase. All the X ray spectra show a broad hump for a wave vector between 0.1 and 0.5 $Å^{-1}$; this is characteristic of the AOT/water system [18]. The first and second Bragg peaks can be seen for polymer concentrations of 0.05–3.5%. The relative intensity and the position of the first- and the second-order Bragg peaks for all the samples investigated (P*X*:*Y*, PS*X*:*Y* and PP25:8 series) are summarized in Table 1. The position ratio (k_2/k_1) of these two Bragg peaks is close to 1:2 and agrees with that expected for an L_α phase.

Normally for a lamellar phase the intensity ratio between the first- and second-order peaks (I_2/I_1) is expected to be less than 1 [19]; however, for the present data it is found that the intensity of the first peak decreases with polymer concentration ($I_2/I_1 > 1$). For the sample with 8.0 wt% PDMAA the first peak has disappeared, and only the second-order peak can be detected. This anomalous behavior has previously been reported for the AOT/water system [18], and was explained in terms of a modulation by the bilayer form factor. In contrast to the present samples, this observation was made at a higher AOT concentration, corresponding to a weight fraction of AOT between 0.35 and 0.45. From Table 1 it is clear that PDMAA shifts the occurrence of this effect to a lower total AOT content. Thus, it seems that addition of PDMAA reduces the water content in the lamellar phase.

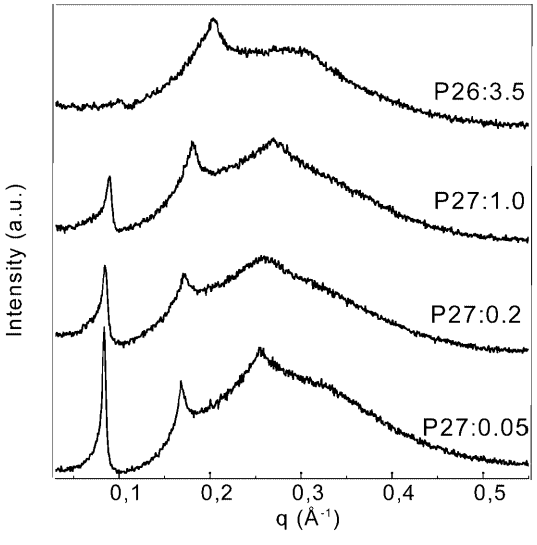

Fig. 4. Typical small-angle X-ray scattering (*SAXS*) diffraction patterns for the P*X*:*Y* samples, where *X* and *Y* are the amounts (% w/w) of AOT and PDMAA, respectively

Table 1. The Bragg peaks (k_1, k_2), their ratio (k_2/k_1) and the ratio of the intensities (I_2/I_1) found in the small-angle X-ray scattering spectra for the different series of samples (P*X*:*Y*, PS*X*:*Y*, and PP25:8, where *X* and *Y* are the amounts of Aerosol OT (*AOT*) and poly(*N*,*N*- dimethylacrylamide) (*PDMAA*), respectively, S indicates that fluorescent probe *N*-(2-aminoethyl)-5-(dimethylamino)naphthalene sulfonamide was added at a concentration of $1.63 \pm 0.09 \times 10^{-3}$ wt% and *PP* means that the sample has the fluorescence-labeled polymer)

Sample	k_1 ($Å^{-1}$)	k_2 ($Å^{-1}$)	k_2/k_1	I_2/I_1
P27:0.05	0.083	0.172	2.08	0.3
P27:0.1	0.083	0.173	2.09	0.3
P27:0.2	0.085	0.174	2.04	0.4
P27:1.0	0.088	0.180	2.04	0.6
P26:3.5	0.098	0.203	2.07	5
PS27:0.1	0.081	0.166	2.05	0.2
PS27:0.2	0.083	0.168	2.03	0.3
PS27:1.0	0.087	0.177	2.04	0.6
PS26:3.5	0.097	0.199	2.06	3
PP25:8.0		0.234		

From the positions of the first- and second-order Bragg peaks the repeat distance (or long period), *d*, of the lamellar phase can be obtained. It can be seen in Fig. 5 that *d* decreases with increasing polymer concentration. Two scenarios can explain this observation. In the first one, the polymer chains are located between the lamellae and by using *d* in combination with the sample composition, information about the thickness of the AOT bilayer, d_0, and of the water bilayer, d_w, can be obtained from geometrical considerations, $d_0 = \phi d$ [20]. Here ϕ is the AOT volume fraction, and the long period, *d*, is the sum of d_0 and d_w, $d = d_0 + d_w$. A decreased d_0 implies that the average headgroup area, *A*, increase, since $A = 2V_a/d_0$. (V_a, the volume of an alkyl chain of the surfactant molecule, is estimated to be 639 $Å^3$ [21]). The calculated d_0, *d*, and *A* values are shown in Table 2; from these, a decrease of the bilayer thickness, and so an increase of the average area per polar headgroup, is obtained. This behavior has previously been observed for the PEG/SDS/water system [4] but in that case the polymer is partially associated to the surfactant bilayer. The commonly observed association between single-chain ionic surfactants and nonionic weakly polar polymers has an electrostatic origin: ionic surfactant self-assembly has an entropic penalty related to the counterion distribution which is partly eliminated on polymer/surfactant association. This is not likely to be

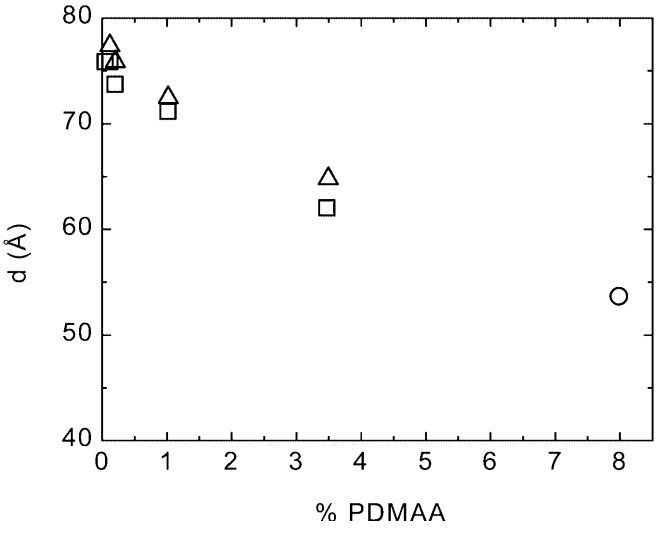

Fig. 5. The long period, d, from SAXS diffractograms, as a function of the polymer concentration. The *squares* correspond to data from PX:Y samples (P26:3.5; P27:1.0; P27:0.2, and P27:0.05), the *triangles* correspond to PSX:Y samples (PS26:3.5, PS27:1.0, PS27:0.2 and PS27:0.01), and the *circle* is obtained from the PP25:8 sample with 25 wt% AOT and 8 wt% PDMAA-*co*-pyrenilmethyl methacrylamide. X and Y are the amounts (% w/w) of AOT and of PDMAA, respectively, and S was present at a concentration of $1.63 \pm 0.09 \times 10^{-3}$ wt%)

Table 2. The long period, d, the thickness of the bilayer, d_0, and the headgroup area, A, as calculated with the assumption that the PDMAA can enter the lamellar phase in the samples PX:Y, PSX:Y, and PP25:8

Samples	d (Å)	d_0 (Å)	A (Å^2)
P27:0.05	75.9	19.2	66.7
P27:0.1	75.9	19.2	66.7
P27:0.2	73.7	18.6	68.7
P27:1.0	71.2	17.8	71.7
P26:3.5	62.0	15.2	84.3
PS27:0.1	77.4	19.5	65.6
PS27:0.2	75.9	19.2	66.5
PS27:1.0	72.5	18.1	70.5
PS26:3.5	64.8	15.9	80.5
PP25:8.0	53.7	12.5	102.2

the case in the present systems since AOT and PDMAA were found not to associate (from conductivity). Another effect that could be expected if large macromolecules dissolve in the lamellar phase is a broadening of the diffraction peaks. This is so because the thickness of the water layer is expected to increase at the point where macromolecules are located. In our data no such broadening is detected and thus there is no indication of polymer localization in the lamellar phase. However, the primary beam affects the width of the diffraction peaks, and unfortunately (after desmearing the data) the widths of primary beam and the diffracted peaks are similar and so it is difficult to obtain quantitative data in order to determine if there is a broadening of the peaks due to polymer.

In summary, from this discussion it seems that the polymer chains are not located between the bilayers, and in combination with the observation that PDMAA could induce a phase separation we regard this first scenario is less likely. Before we proceed, we note that extrapolation to 0 wt% polymer in Fig. 5 gives $d = 75.5 \pm 0.6$Å, from which a value of the bilayer thickness, d_0, of 19 ± 2 Å can be obtained; this is totally in agreement with that previously reported [22].

In the second scenario, PDMAA forms a new phase since the polymer chains are too large to enter the lamellar phase without being significantly compressed. The free-energy loss that such compression would bring about is larger than that following phase separation. The model proposed by Zhang and Linse [9] describes this kind of systems in terms of the free-energy difference between a one-phase and a two-phase system. They concluded that the reduction of the chain length would lead to a reduction in the free energy gained. In our model, the AOT is concentrated in one phase and the polymer is concentrated in the other phase (segregation), so d_0 is expected to remain constant ($d_0 = 19.2$ Å), while d_w (and d) would decrease by osmotic compression from the PDMAA-rich phase.

In conclusion, the SAXS data give indirect evidence of two phases in equilibrium since the AOT-rich phase becomes osmotically compressed by a PDMAA-rich phase. While only the lamellar AOT-rich phase has a structure that can be observed directly, the other phase (containing the polymer) is likely to be isotropic.

^{2}H NMR

We used ^{2}H NMR to measure the average anisotropy that water (D_2O) molecules experience during their motion through the solution [23]. In short, in the present case this experiment monitors the fraction of water molecules that are located close to a bilayer and their average anisotropy; it is known that water molecules, in general, exchange rapidly on the NMR timescale between the hydrated and the "free" states. Therefore, such NMR data convey information about the composition of an anisotropic phase, like the lamellar phase. In particular, however, it provides information on the presence of different phases with different degrees of anisotropy; notably an isotropic phase, like an isotropic solution, gives a narrow singlet of high amplitude in contrast to the doublet (quadrupole splitting) of an anisotropic phase. A singlet can also arise for an anisotropic phase with very small microcrystallites; however, in this case there is a broadening of the signal. This implies that the D_2O spectra can be used to identify various phases. This is particularly convenient

in samples containing more than one phase in equilibrium, but where macroscopic phase separation for some reason is not possible to achieve. One example could be the lamellar phase in coexistence with an isotropic phase. In this case the spectrum is composed of two subspectra superimposed, where the central line is from the isotropic phase, while the doublet stems from the lamellar phase.

The ^{2}H NMR spectra for four samples with the same AOT/D_2O ratio but with polymer concentrations varying from 0 to 7.5 wt% are shown in Fig. 6. From these spectra we can deduce that samples containing polymer have two phases. One phase is clearly anisotropic (splitting), while the other phase results in a singlet. This central peak can most likely be attributed to an isotropic phase; an anisotropic phase consisting of small fragments with random orientation is less likely since the singlet is very narrow and occurs for a large range of polymer concentrations. At low concentrations of AOT, a singlet has been found to correspond to an anisotropic phase [24]; however, in that case the SAXS data contain additional information about the anisotropic nature of that sample. Since the present SAXS spectra show only one kind of structure, we conclude that the other phase is isotropic. The extent of quadrupole splitting, Δ, from the ^{2}H NMR experiment is shown in Fig. 7a as a function of polymer concentration. We can correlate this experimental splitting with information on the anisotropic phase through Eq. (1) [9]:

$$\Delta = n\upsilon_Q s(1 - X_{D_2O})/X_{D_2O} \quad (1)$$

Here ν_Q (220 Hz for deuterium in a water molecule) is the effective quadrupolar splitting constant, n is the average hydration number of the amphiphilic molecules in the bilayer, s is the order parameter, and $X_{D_2O}$is the mole fraction of water in the phase of interest. If we regard all parameters except X_{D_2O} as being constant we can combine the data from the ^{2}H NMR experiment with information from the SAXS measurements. Δ is plotted as a function of $(1 - X_{D_2O})/X_{D_2O}$ from the SAXS measurements in Fig. 7b. The latter was calculated from the long period, d, with the assumption that all the AOT was within the lamellar phase and that the other phase contains only PDMAA dissolved in water. A straight line could be nicely fitted to the data, which is strong evidence that our assumption regarding the composition

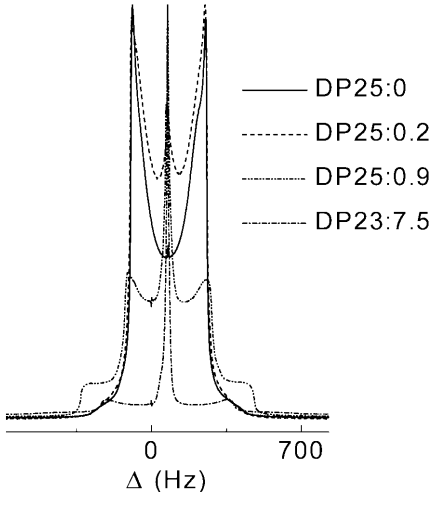

Fig. 6. ^{2}H NMR spectra from four samples that contain AOT and polymer. The AOT:PDMAA concentrations (wt%) are indicated in the figure

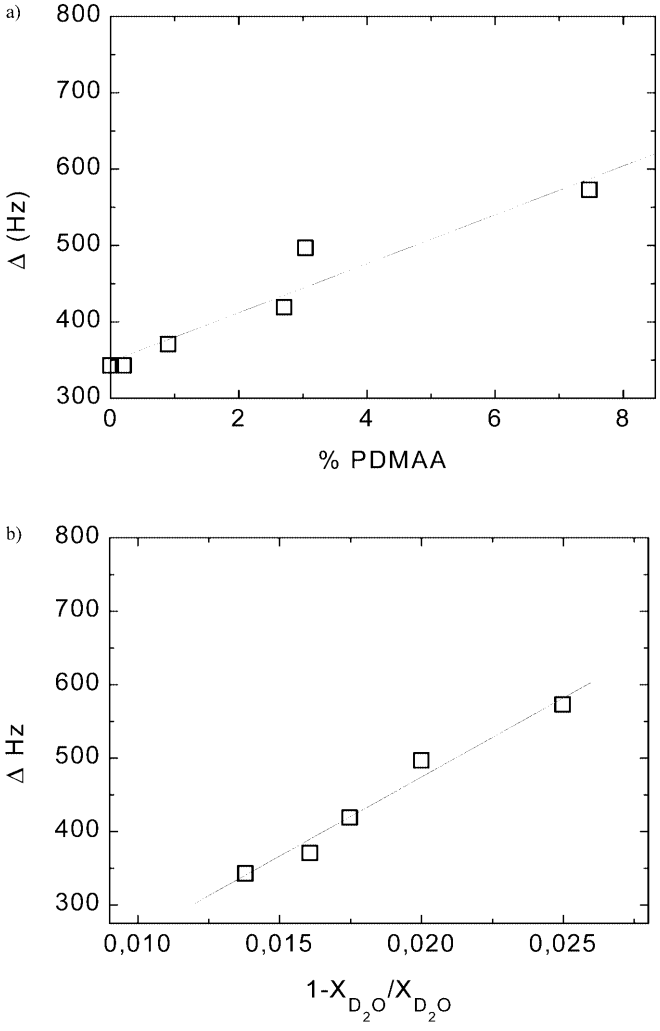

Fig. 7a,b. Quadrupolar splitting, Δ, from the ^{2}H NMR spectra of the D_2O/AOT/polymer samples. **a** Δ as a function of the polymer concentration. **b** Δ as a function of $(1 - X_{D_2O})/X_{D_2O}$, the mole fraction of anisotropic water contained in AOT + D_2O lamellae as deduced from SAXS measurements in these samples. The *line* describes the best linear fit to the data. The samples are DP25:0, DP25:0.2, DP25:0,9, DP25:2,7, DP27:3,0 and DP23:7,5, where the first and the second numbers are the amounts (% w/w) of AOT and PDMAA, respectively

of the samples, with one lamellar phase in equilibrium with a polymer-rich phase, is correct.

Fluorescence

It is well known that the medium can affect the electronic excited state of a molecule. In such cases the emission spectra can provide us with information about the environment (i.e., polarity or microviscosity) where the molecule is located. This property makes the fluorescence technique useful for studying microheterogeneous systems. With this purpose two kinds of experiments may be performed: to dissolve a fluorescent probe in the systems and to use a label, which is covalently bonded. In this work we used these two tools in order to determine where the polymer is located in our lamellar system.

The fluorescent probe S has an emission spectrum sensitive to the polarity of the environment [25]; this is shown in Fig. 8a, where the ratio of the intensity at 497 and 539 nm (I_{497}/I_{539}) is depicted for different mixtures of water and dioxane. This ratio increases from 0.37, for the solution in water, to 2.16, for the solution in dioxane. In addition the fluorescence ratio for different AOT/water mixtures is presented in Fig. 8a; in this case, independent of the composition, $I_{497}/I_{539} = 0.89 \pm 0.03$. This implies that in the last system the probe is always in the same environment, a medium with a polarity intermediate between that of water and dioxane. The interfacial region in the bilayer close to the AOT headgroups could, for instance, provide such an environment.

Once we know where the probe is located in the lamellar system, it should be significant to determine the effect of the polymer on the fluorescence spectrum. Figure 8b shows that the addition of the polymer had a negligible influence on the I_{497}/I_{539} ratio, although a small increase of the fluorescence ratio can be discerned for the highest polymer concentrations. In contrast, it can be noted that when S is dissolved in dimethylpropionamide (the monomer analog of PDMAA), the fluorescence ratio is significantly higher than in water ($I_{497}/I_{539} = 1.32$).

Finally, the probe was added to samples containing both AOT and PDMAA (PSX:Y set). It was found that the fluorescence ratio was always 0.90 ± 0.01 independent of the composition, the same ratio we found for the AOT/water system, indicating that S and PDMAA are not located close to each other. From this experiment we can conclude that the polymer is not near the bilayer, in agreement with our model.

As previously mentioned, in our study we also used a pyrene-labeled polymer (PDMAA*). This kind of experiment has the advantage that the information we obtain is about the medium where the polymer is dissolved. The photophysics of pyrene is very well known;

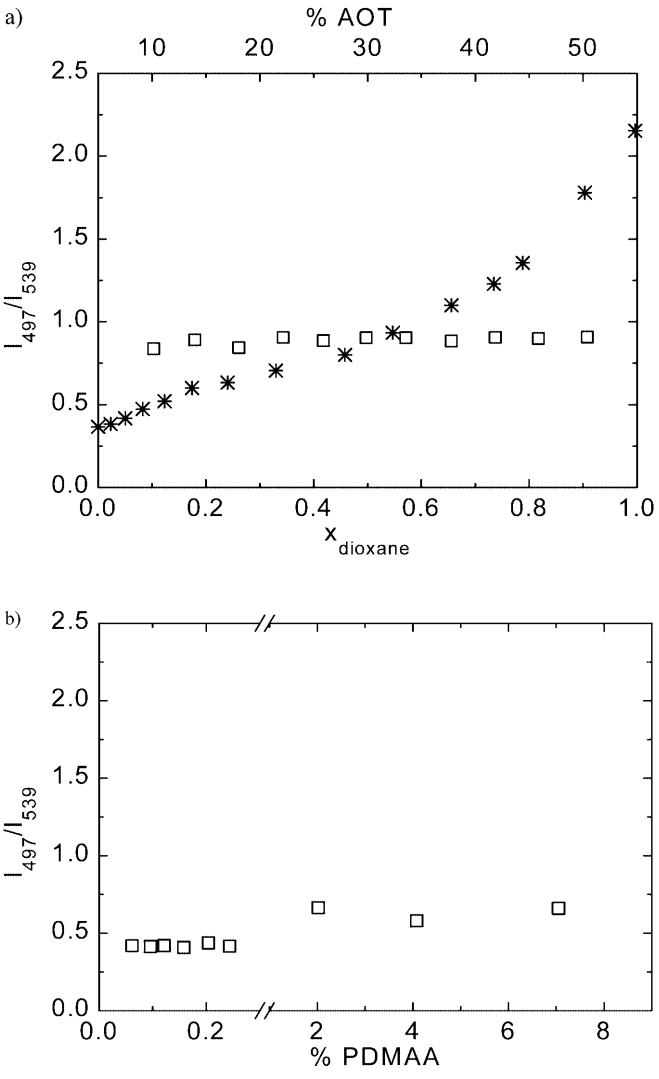

Fig. 8a,b. Ratio of the vibrational peaks located at 497 and 539 nm, respectively, of the fluorescence spectra of S, at 25 °C with excitation at 325 nm (slit widths were 4 nm both for the excitation and the emission monochromators). **a** The I_{497}/I_{539} ratio presented either as a function of the molar fraction of dioxane in dioxane/water ($x_{dioxane}$) (*stars*) or as a function of the weight percent AOT in water (*squares*). The concentration of S was kept constant at 0.0016 wt%. **b** The I_{497}/I_{539} ratio as a function of the PDMAA concentration in water. The concentration of S was kept constant at 0.0013 wt%

the fluorescence ratio of the I and III (I/III) vibronic bands increases with the polarity [26]. This behavior is depicted in Table 3, where we have summarized data for the pyrene emission in different environments: as a probe in a micellar solution (oil medium), dissolved in water, and as PDMAA* at different concentrations in water or in an AOT/water system (PP25:8). No excimer emission that could distort the result was detected since the fluorescence probe concentration was kept very low in all the samples. The fluorescence ratio of pyrene

Table 3. The ratio of intensities of the first (376 nm) to third (388 nm) vibrational peaks in the pyrene spectra for different solutions: water, a micellar solution of AOT, water solutions of the labeled polymer (PDMAA*), and sample PP25:8 containing 25 wt% AOT and 8 wt% PDMAA*

Sample	I/III
Micellar solution[a]	1.29
Water	1.84 [27], 1.87 [28]
0.96% PDMAA*	1.73
2.00% PDMAA*	1.92
3.81% PDMAA*	2.01
5.56% PDMAA*	2.05
9.37% PDMAA*	2.05
PP25:8	2.08

[a]1% AOT and 1.8×10^{-6} M label

anchored to the polymer is larger than in pure water and in the micellar environment. In the lamellar system the chromophore, and therefore the polymer, is located in the same environment as without AOT, i.e., in an aqueous medium; the only effect of the presence of AOT on the pyrene fluorescence ratio is to increase it, as if the polymer concentration were larger than the initial concentration. This strongly supports our model where the polymer is expelled from the lamellae, and so its effective concentration is larger than the macroscopic concentration.

Conclusion

AOT and PDMAA show no association in an aqueous solution. Instead, at least if the polymer coils are large compared to the thickness of the water domains in the lamellar phase, two separate phases in equilibrium are formed. However, since the viscosity is rather high and the difference in density between the phases is small, macroscopic phase separation could not be achieved. Instead small domains (less than 10 μm) of the isotropic polymer-rich phase are interspersed within the anisotropic lamellar AOT-rich phase. Since there is segregation between polymer and surfactant, the polymer reduces the repeat distance of the lamellar phase by osmotic compression. A theorerical study about this effect will be analyzed in forthcoming work.

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References

1. Bickel T, Jeppesen C, Marques CM (2001) Eur Phys J E 4:33
2. Nylander T, Ericsson B (1997) In: Froberg SE, Larson K (eds) Food emulsions, 3rd edn. Dekker, New York, pp
3. (a) Radlinska EZ, Gulik-Krzywicki T, Lafuma F, Langevin D, Urbach W, Williams CE (1997) J Phys II 7:1393; (b) Radlinska EZ, Gulik-Krzywicki T, Lafuma F, Langevin D, Urbach W, Williams CE, Ober R (1995) Phys Rev Lett 74:4237
4. Ficheux MF, Bellocq AM, Nallet F (1995) J Phys II 5:823
5. Demé B, Duboid V, Zemb T, Cabane B (1996) J Phys Chem 100:3828
6. Ligoure C, Bouglet G, Porte G, Diat O (1997) J Phys II 7:473
7. Ligoure C, Bouglet G, Porte G (1993) Phys Rev Lett 71:3600
8. Kekicheff P, Cabane B, Rawiso M (1984) J Colloid Interface Sci 102:51
9. Zhang K, Linse P (1995) J Phys Chem 99:9130
10. Ficheux MF, Bellocq AM, Nallet F (1997) Colloids Surf A 123–124:253
11. Freyssingeas E, Antelmi D, Kékicheff P, Richetti P, Bellocq AM (1999) Eur Phys J B 9:123
12. Shea KJ, Stoddard GJ, Shavelle DM, Wakui F, Choate RM (1990) Macromolecules 23:4497
13. Ren B, Gao F, Tong Z, Yan Y (1999) Chem Phys Lett 307:55
14. http:// www.aist.go.jp/RIODB/SDBS/ (2000)
15. Trossarelli L, Meirone M (1962) J Polym Sci 23: 445
16. Rogers J, Winsor PA (1969) J Colloid Interface Sci 30:247
17 Porte G, Appel J, Bassereau P, Marignan J (1989) J Phys (Paris) 50:1335
18. Nallet F, Laversanne R, Roux D (1993) J Phys II 3:487
19. Pershan PS (1993) In: Shmueli U (ed) International tables for crystallography. Kluwer, Dordrecht, p 441
20. Luzzati V (1968) In: Chapman D (ed) Biological membranes. Academic, London, p 71
21. Magalhaes M, Puisol D, Ramia ME, Figueiredo Neto AM (1998) J Chem Phys 108:3835
22. Fontell K (1973) J Colloid Interface Sci 44:318
23. Halle B, Wenneerström H (1981) J Chem Phys 75:1928
24. Chidichimo G, la Mesa C, Ranieri GA, Ternzi M (1987) Mol Cryst Liq Cryst Sci Technol Sect B 150:221
25. Li Y-H, Chan L-M, Tyer L, Moody RT, Himel CM, Hercules DM (1975) J Am Chem Soc 97:3118
26. Kalyanasundaram K, Thomas JK (1977) J Am Chem Soc 99:2039
27. Kalyanasundaram K (1987) Photochemistry in microheterogeneous systems (1987) Academic, London
28. Dong D, Winnik MA (1982) Photochem Photobiol 35:17