Polymer Induced Phase Separation in Lyotropic Smectics

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Large water soluble macromolecules can be confined in all proportions into an electrostatically stabilized surfactant lamellar phase without change of the bilayer thickness. Upon progressive addition of salt, the sample phase separates into a polymer-rich and a surfactant-rich lamellar phase. Indeed, at some particular salt concentration, the intermembrane repulsive interaction is no longer sufficient to maintain the polymer coils squeezed into the lamellar structure. The phase separation is generally first order. But we could find a situation where it becomes second order.

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Amphiphilic molecules in aqueous solutions often self-assemble into very large bilayer membranes [1–3] regularly stacked parallel to each other. The resulting lamellar phase is birefringent and shows quasi-long-range smectic order. It has been shown experimentally [4] that for charged bilayers (ionic amphiphiles) in pure water the smectic order is stabilized by strong long-range electrostatic interaction, whereas in high salt brine (few $10^{-1}M$) the electrostatic interaction is screened beyond distances shorter than the smectic periodicity so that the stability of the phase only arises from the much weaker steric repulsion between membranes [5].

On the other hand, the behavior of macromolecules confined into small pores or thin slits (of size much smaller than the natural radius of gyration of the unconfined coil) has been studied theoretically quite long ago [6]. However, experimental realizations of such situations that are convenient for the measurements of relevant quantities are not easy to achieve [7]. So, at the present time, we are not aware of any convincing experimental checks of the theoretical conjecture. However, if some hydrosoluble polymer could be incorporated into the L_α phase with suitable periodicity, one could have a chance to realize a situation somewhat similar to the confinement in infinite slits. But the only appropriate case would be one where (i) the polymer does not penetrate through the bilayers, so that the confinement is effective; (ii) the polymer shows no specific interaction with the membrane so that the strong adsorption regime is avoided. This idea is at the basis of the present study.

We incorporate a large hydrosoluble polymer into an L_α phase made of charged bilayers. If the polymer is effectively confined in between the bilayers, some additional contribution to the effective interaction between the bilayers will come into play. Two different physical situations may arise in the case of a semidilute solution of nonadsorbing polymers trapped in small slits [6].

(i) In the three dimensional regime, the size of the slits is much larger than the three dimensional correlation length ξ; in this case the corresponding free energy of confined polymers consists of a "bulk" contribution and a term associated with the depletion of polymers near the surface.

(ii) In the two dimensional regime, the size of the slits is much smaller than the three dimensional correlation length ξ; the chains are strongly compressed and can be viewed as a two dimensional semidilute solution. The free energy of confined polymers consists now of the work required to compress a spherical blob into a pancake and the work involved in bringing pancake-shaped blobs into contact.

More precisely, the polymer will have a tendency to concentrate where the interlayer spacing is larger (where it is less confined) and conversely to escape from parts of the sample where the interlayer spacing is thinner. So, at fixed solvent concentration, the presence of the polymer should decrease the effective repulsion between bilayers and correlatively increase the smectic compressibility at constant chemical potential $\bar{B}^{-1}$ of the lamellar stacking. Therefore two situations might arise: either (i) the initial interaction between the bilayers is strong enough so that the confinement contribution is incapable to complete it: The sample remains monophasic with a somewhat larger smectic compressibility; or (ii) the initial interaction is small: then the confinement contribution might well overcompensate it so that the sample eventually phase separates into one surfactant-rich–polymer-poor phase and one surfactant-poor–polymer-rich phase.

We proceed in two steps. First, we incorporate various concentrations of the polymer in the electrostatically stabilized phase (strong interaction). We check, using x-ray scattering technique, that the thickness of the bilayers remains unchanged however high the polymer concentration is. We make sure that the polymer neither adsorbs onto the bilayer surface, nor penetrates through the membrane. Second we fix both the bilayer and the polymer concentrations at suitable values and only vary the salt concentration. Doing so, we monitor the decrease of the interlayer interaction: The Bragg singularity (x rays) weakens progressively and ultimately the sample phase separates (two Bragg peaks). For most initial conditions (polymer concentrations), the phase separation is indeed first order. But we could find a situation where it becomes second order.

The L_α phases are obtained from the system CPCL (cetylpyridinium chloride)/hexanol/brine, for which we have the most extensive set of structural data [8]. The salinity of the solvent is varied in the range $0M$ (pure wa-

ter) to 0.22M. The alcohol to surfactant ratio is fixed: $M_{hex}/M_{CPCL}=0.9$, so that the lamellar structure is preserved at all salinities, also the mass fraction of the solvent is kept constant ($M_{brine}=66.75\%$). Polyvinylpyrilidone (PVP) was used as the polymer. Pure water and brine up to 0.5M NaCl concentration are good solvents for PVP [9]. It is a nonionic polymer and does not interact (or only very weakly) with cationic surfactants as CPCL in micellar solution [10]. We use a commercial product. The reported molecular weight is 360000; we measured its weight average molecular weight by light scattering: $M_W=750000\pm10\%$; so the polydispersity is about 2. The radius of gyration is about 60 nm in pure water and 45 nm in 0.22M brine. The overlapping weight concentration c^* is found close to 0.15% in pure water and 0.3% in 0.22M NaCl brine. Thus salt addition only slightly decreases the quality of the solvent. It is important to notice that (i) in all cases the amount of polymer added is much larger than c^*, and (ii) the interlamellar distance is always much smaller than the radius of gyration of free chains. Consequently, in all samples studied, (i) the polymer solution is semidilute and (ii) the chains should be squeezed between the bilayers. With such conditions, we are in a good position to observe the new direct polymer-mediated interaction due to the confinement energy of the chains between flat bilayers. We interpret quantitatively the Bragg peak position q_B (x-ray scattering) in terms of the dry thickness of the bilayers δ:

$$q_B=(1-\phi_d)2\pi/\delta, \tag{1}$$

where ϕ_d is the volume fraction of the solvent.

We were able to incorporate PVP into the L_α in pure water system up to a relative proportion $M_{PVP}/M_{H_2O}=60\%$. The sample remains monophasic, transparent, very viscous, and birefringent. The position of the first Bragg peak is in accurate agreement [Eq. (1)] with the picture where the polymer is distributed into the aqueous solvent only, and leaves the bilayers dry thickness constant ($\delta=2.5\pm0.04$ nm) and identical to that measured in the L_α phase free of polymer. This experimental fact proves that PVP does not adsorb onto the bilayers' surface and does not penetrate through their hydrophobic cores. So the conditions of confinement are well satisfied. This result allows us to suppose in the following that the polymer does not affect the bilayers of the lyotropic smectic CPCL/hexanol neither in pure water nor in brine.

Then we investigate three series of samples of constant compositions in amphiphiles and incorporate, respectively, 0%, 3.2%, and 6.2% mass fraction of the PVP as a function of salinity. All samples were kept in closed tubes at constant temperature $T=20\,°C$, and observed over long durations. The first one (0% polymer) is taken as the reference series. Figure 1 shows the x-ray scattering patterns for three salinities (pure water, 0.05M NaCl brine, and 0.22M NaCl brine). The first sample (pure
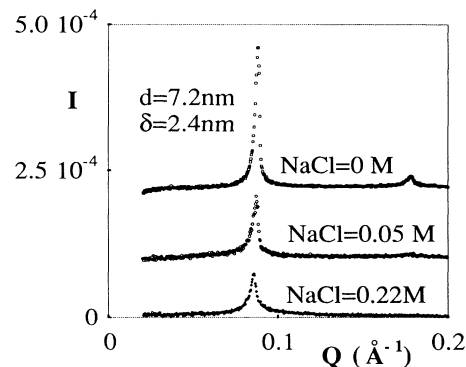

FIG. 1. Intensity vs q (Å^{-1}) curves of the reference series: CPCL/hexanol/brine L_α phase (absence of polymer) for three different salinities (0M, 0.05M, and 0.22M).

water) exhibits both the first and second order harmonics of the structure factor. The existence of the two harmonics confirms the lamellar structure. The second sample (0.05 NaCl brine) exhibits the first and the second harmonic too; however, note the broadening of these harmonics, especially of the second order peak. The last sample (0.22M NaCl) exhibits only the first Bragg singularity, being much softer than that of the pure water sample.

In terms of the current theory of scattering by smectic media [11], we expect $I\sim(q-q_B)^{-x}$,

$$\eta=\frac{q_B^2 k_B T}{8\pi(K\bar B)^{1/2}} \tag{2}$$

with $x=1-\eta$, rather than $2-\eta$, because of the powder averaging. q_B denotes the position of the Bragg peak. $\bar B$ is the compression modulus at constant chemical potential, d is the smectic periodicity, and K is the elastic modulus of bending. The value of η is directly related to the interaction between the bilayers. A qualitative comparison of the theoretical relation [Eq. (2)] with our experimentally obtained data is shown in Fig. 2. The figure shows the large difference in slope which is indicative of the difference in the interaction between membranes with similar interlamellar spacings but separated by different solvent (water, polymer solution in water, brine). The weaker is the repulsive interaction; the smaller is the exponent x.

By comparing curve a and curve c in Fig. 2, it appears that, at identical dilution, η is less in pure water than in brine, in agreement with the relative strength of electrostatic versus Helfrich's interactions. Accordingly for intermediate salinities (between 0M and 0.22M) we observe intermediate scattering profiles. These preliminary experiments without polymer confirm that increasing salt addition monotonically weakens the effective interlayer interaction [4].

In Fig. 3 are representations of the scattering patterns of the series with 3.2% PVP incorporated. In the range 0M NaCl to 0.06M, the samples are monophasic,
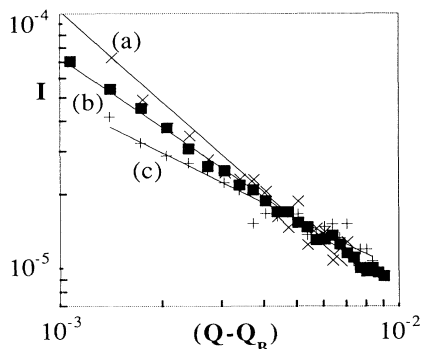
FIG. 2. Profiles of the first harmonic for three different samples with similar interlamellar spacing: curve a: $0M$ NaCl, PVP 0%; curve b: $0M$ NaCl, PVP 3.2%; and curve c: $0.1M$ NaCl, PVP 0%. The plots are on a log-log scale. The figure shows the large difference in slope: the smaller the slope, the weaker the repulsive interaction between membranes.

birefringent, and slightly cloudy. The scattering patterns are qualitatively similar to those of the polymer free series. However, we note that the Bragg singularity is weaker than that of the polymer free samples of the same salinity. This is confirmed by comparing curve a and curve b in Fig. 2. This reveals the extra softening contribution to $\bar{B}$, due to the polymer confinement.

In the range $0.07M$ NaCl to $0.125M$ NaCl the samples still appear monophasic and birefringent, but they are more transparent and bluish. We observe (i) strong scattering at small angle, (ii) broadening of the Bragg peak; at $0.08M$ salinity the singularity of the first Bragg peak is killed off and replaced by a rounded maximum as clearly revealed by Fig. 3(a), where the scattering patterns of the sample without salt and the sample at $0.08M$ salinities are plotted. (Note that for convenience, the $0M$ NaCl intensities have been divided by 4.) (iii) Between $0.09M$ and $0.11M$ the Bragg maximum continuously splits in two and reveals the coexistence of two lamellar phases of different pitches. At still higher salinities the maxima separate more and more and progressively sharpen. So finally, at $0.15M$, the amphiphile poor L_α phase has a pitch too large to be observed in the q range of the experiment. We observe therefore only the Bragg peak of the amphiphile rich lamellar phase which has a pitch indeed smaller than that of the initial homogeneous smectic sample. These experimental results demonstrate definitely that a second order phase separation occurs at some particular salt concentration between $0.08M$ and $0.09M$, as explained below.

For a second order phase separation, the corresponding susceptibility (the smectic compressibility $\bar{B}^{-1}$) diverges. Therefore, η increases and becomes larger than 1, so that the exponent $-x = -(1-\eta)$ becomes positive and the Bragg singularity vanishes, replaced by a rounded maximum as observed in our experiment [see Fig. 3(a)]. The intensity scattered at low $q (q \ll q_B)$ is also related to the
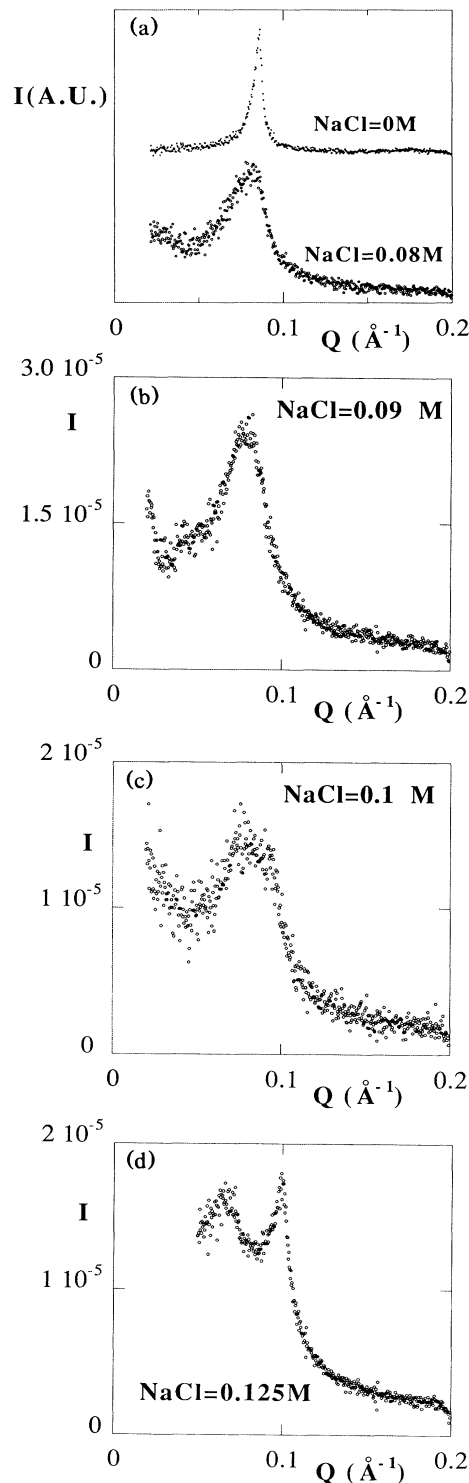

FIG. 3. Intensity vs q (Å^{-1}) curves in the vicinity of the second order phase separation of the series of samples containing 3.2% PVP in weight. Note that in (a) the intensity of the pure water sample has been divided by 4 for convenience. A second order phase separation occurs between $0.08M$ and $0.09M$ NaCl.
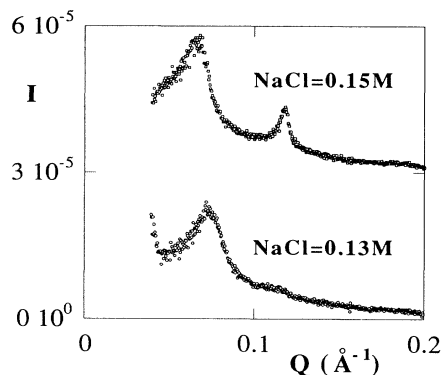
FIG. 4. Intensity vs q (Å^{-1}) curves of the series of samples containing 6.2% PVP in weight. A first order phase separation occurs at $0.13M$ NaCl.

smectic compressibility: $I(0) \approx k_B T(\bar{B})^{-1}$, and therefore increases dramatically [12]. Close to the transition salinity, the two distinct lamellar phases have very similar smectic spacing. These three experimental observations: (i) rounded maximum, (ii) increase of the intensity at low q and (iii) continuous splitting of the Bragg peaks at the transition salinity prove that the phase separation is second order. It should be noticed that, in the present case, the three dimensional correlation length $\xi \sim R_G \times (c^*/c)^{3/4} = 5.5$ nm equals approximately the size of the slits (5 nm). Thus, the situation is intermediate between the two dimensional and the three dimensional regimes of confined polymers.

This general behavior, compared to that of the polymer free series, confirms that the free energy contribution due to the polymer confinement is capable of monitoring a phase separation in two lamellar phases of different compositions: the chains spontaneously concentrate where they are less confined, i.e., in the amphiphile poor L_α phase.

However, the question arises whether the phase separation is intrinsically second order or rather it corresponds to a critical point of an otherwise first order transition. So, we have incorporated in the references samples about twice as much polymer ($M_p = 6.2\%$). X-ray scattering data show a single lamellar phase ($d \approx 7.65$ nm) at salinities less than $0.13M$. At $0.13M$ salt concentration (see Fig. 4), a slight shoulder appears on the right hand side of the main Bragg peak revealing the apparition of a very small proportion of an amphiphile-rich phase (smaller smectic pitch). Increasing the salinity leads to an increase of this proportion and correlatively, the corresponding first order Bragg peak grows. In this case, contrary to the previous one, the two phases have very different pitches at the transition. We thus conclude that the phase separation is clearly first order. Therefore $M_P = 3.2\%$ corresponds to a particular case where the composition happens to be close to the critical conditions, so that the general behavior observed is second order. This is the first time, to our knowledge, that a second or-

der phase separation is found in polymer surfactant systems. Very recently a second order phase separation in a surfactant lamellar system has been reported [13].

In conclusion, we have achieved an experimental realization of a polymer confined in a lyotropic smectic stacking having a pitch much smaller than the average size of the free macromolecule. The comparison with the polymer free reference series clearly reveals the polymer specific contribution to the effective interaction between bilayers. At some point, the attractive contribution due to the confinement is capable of inducing a L_α/L_α phase separation. Even more, this phase separation becomes second order for some suitable polymer concentration. However, our study remains qualitative. On the one side, the theoretical work of Brooks and Cates [14] seems appropriate to our experimental situation. On the other side, the quantitative treatment of the Bragg singularity should allow an indirect measurement of $\bar{B}$ (provided that the monophasic configuration of the sample is well defined: true powder or fully oriented sample). So, it is in principle possible to go well beyond the present qualitative analysis. Such a more quantitative investigation is under current progress.

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