Polyelectrolyte-mediated undulation of surfactant bilayers

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We studied the effect of the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) on the highly dilute lamellar L_α phase formed by the nonionic surfactant triethylene glycol monodecyl ether ($C_{10}E_3$) in water. Upon addition of PDADMAC, light scattering shows nonlamellar order, indicating the formation of strongly undulated bilayer structures with repeat distances as large as 200 nm. The effect is supposed to originate from attractive bridging forces between polyelectrolyte-covered membranes. [S1063-651X(98)03512-0]

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In a binary aqueous solution surfactant molecules often self-aggregate into stacks of extended bilayer membranes [1]. It has been theoretically predicted [2–4] that the incorporation of polymer into such lamellar phases can affect the elastic properties of the membranes, thereby influencing their phase stability and the state of surfactant organization. Experiments have shown [5–13] that the behavior of multicomponent systems strongly depends on the specific interactions between the polymer and bilayer. Adsorbing polymers can directly alter the properties of the membranes, whereas for nonadsorbing polymers the behavior is determined by excluded volume interactions. Confinement effects become important when the interlamellar spacing and polymer coil size are comparable. The different types of interaction have been addressed in different experimental situations but, thus far, in our opinion no comprehensive interpretation of the experimental findings has been given, and further studies are due. With few exceptions [8] most experimental studies focused on concentrated surfactant systems with small interlamellar spacings (≤ 30 nm). A disadvantage is the long equilibration time necessary for preparing spatially homogenous samples.

The situation changes when polyelectrolytes are used instead of neutral polymers. Due to their favorable solubility in water and large radii of gyration, confinement effects may already be expected for highly diluted systems. However, long-range electrostatic interactions will play a crucial role in stabilizing the membrane system. In order to eliminate strong ion-ion interactions between the membrane and polyelectrolyte, bilayer systems formed by nonionic surfactants have to be used. For such systems a low affinity toward polyelectrolytes is generally assumed [8].

Dilute lamellar L_α phases with interlamellar spacings of several hundreds of nm are well known [14,15]. These phases are stabilized by long-range repulsive electrostatic forces or steric repulsion, originating from thermal fluctuations of the membranes [16], and can be easily studied by light scattering techniques [17]. Undulation forces dominate when, first, the membranes are flexible or, in terms of the bending modulus, $\kappa \sim k_B T$, and, second, electrostatic forces are absent or screened out. This condition is satisfied for nonionic surfactant systems. It has to be considered, however, that the polyelectrolyte switches on electrostatic interactions which will compete with undulation forces. The binary system triethylene glycol monodecyl ether ($C_{10}E_3$) water, displaying an L_α phase of stacked bilayers below 30 °C which is stable down to about 1 wt % of $C_{10}E_3$ [18], appeared ideally suited for the experiments. We have investigated various cationic and anionic polyelectrolytes, and observed either adsorbing or nonadsorbing behavior, respectively.

This paper reports a study of the structural changes associated with the incorporation of quaternary ammonium based cationic polyelectrolytes. The polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) [19] was synthesized as described in Ref. [20]. The polymer's repeat unit (bearing on effective charge) essentially consists of a nitrogen containing five membered heterocyclus. The monomer length and molecular weight are 0.55 nm and 161.5, respectively. The molecular weight (M_n) of the investigated samples ranged between 3.1×10^4 and 4.5×10^5 with a polydispersity index M_w/M_n between 1.4 and 1.6. Except for the lowest molecular weight sample, the polymer concentrations in the experiments were within the semidilute region. In the absence of salt, the chains adopt a wormlike conformation where the radius of gyration depends strongly on the ionic strength given by the polyelectrolyte concentration. $C_{10}E_3$ is provided by Fluka. The state of order of the mixed surfactant-polymer-water system was studied by visual inspection in a thermostatic water bath and, more quantitatively, by back scattering of light with a modified two-beam UV/VIS spectrometer (UVIKON 931, Kontron) [17]. The surfactant volume fraction was between $\Phi = 0.015$ and 0.045. The standard temperature was 28.8 ± 0.1 °C. The samples were contained in 10-mm quartz cuvettes. All surfactant and polymer solutions were prepared with milli-Q quality water. The pH remains neutral throughout the whole study without the use of any buffer. The ternary mixtures were obtained after stepwisely dissolving the appropriate amount of concentrated polymer solution

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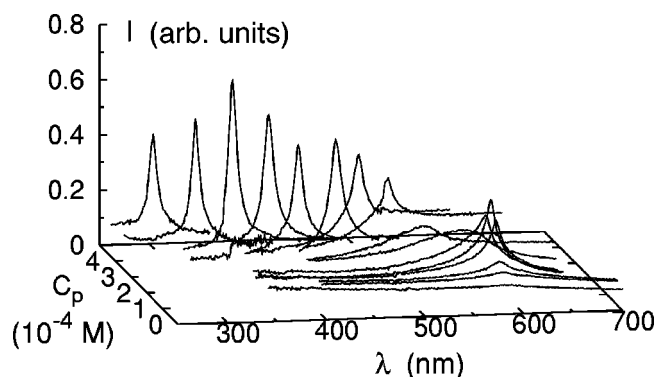*Author to whom correspondence should be addressed.

FIG. 1. Light scattering spectra of a surfactant solution (initial concentration $\gamma_0 = 1.43$ wt %) in relation to the amount of added PDADMAC ($M_n = 1.62 \times 10^5$, molar concentration of monomer units C_p in the mixture).

(1.5×10^{-2} monomole/L) in the surfactant solutions. In most cases the spectra became stable within 15 min.

The highly dilute L_α phase is transparent, birefringent, slightly turbid, and exhibits iridescence. Figure 1 displays a set of light spectra, obtained for an initial surfactant concentration of $\gamma_0 = 1.43$ wt %, and increasing amounts of PDADMAC. The primary effect of adding the polymer is a strong increase in intensity of the weak reflection at $\lambda_{max} \sim 580$ nm, accompanied by a marginal shift toward smaller wavelengths and generally decreasing turbidity of the solutions. Similar effects can be observed when ionic surfactants are added to undulation stabilized L_α phases [8,21]. Coulombic repulsions due to the adsorbed ionic surfactants lead to an increased state of order of the stack of membranes (an increase of intensity) and to a flattening of the undulating membranes (a decrease of interlamellar spacing). The present observation suggests that at first a fraction of PDADMAC up to $C_p \cong 1 \times 10^{-4}$ M adsorbs onto the bilayer (see also Fig. 3). This amount is low, corresponding to about one PDADMAC monomer unit per 500 surfactant molecules in the bilayer. The driving force for adsorption might be the weak ion-dipole interaction between the quaternary ammonium ions and the ethyleneoxide oxygens.

Upon further polymer addition, the Bragg peak vanishes and becomes replaced by a broad maximum which dramati-
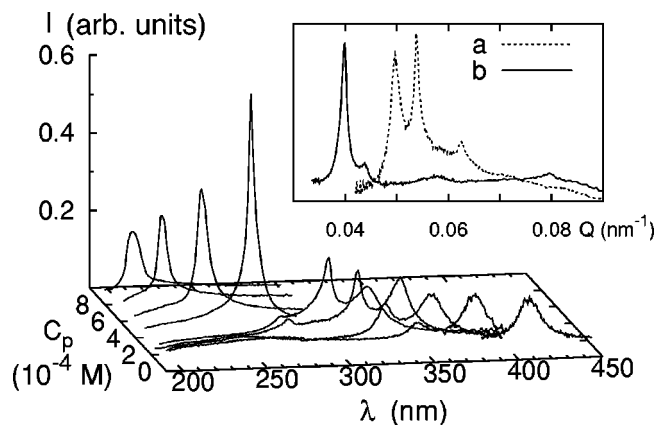

FIG. 2. Effect of adding PDADMAC ($M_n = 1.62 \times 10^5$) on light spectra for a sample with $\gamma_0 = 3.12$ wt %. The inset shows two enlarged single spectra converted to a Q scale. a was measured 1 h after polymer addition, b after five days.
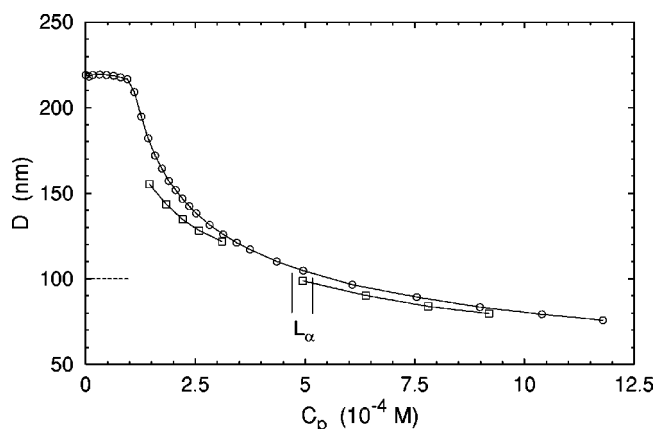

FIG. 3. Characteristic periodic spacing D vs PDADMAC ($M_n = 1.62 \times 10^5$) concentration C_p for samples of low ($\bigcirc$, $\gamma_0 = 1.43$ wt %) and high ($\square$, $\gamma_0 = 3.12$ wt %) initial surfactant concentration. $- - -$, theoretical spacing of the L_α phase at 3.12 wt %.

cally shifts to shorter wavelengths. At the same time the samples become turbid again, and eventually phase separate macroscopically (after about two days) into a turbid solution on the top and a clear bottom phase. For still higher polymer concentrations a sharp peak reappears, and continues to shift toward shorter wavelengths until it leaves the accessible wavelength range. The linewidth of the peaks, ΔQ, is around 10^{-3} nm^{-1}, indicating long-range order with a correlation length $L = \pi / \Delta Q$ of a few μm. The shape of the spectra does not change in the course of at least five days after polymer addition. In some samples a second order reflection was found, confirming the lamellar structure. The described scenario is reproduced for all molecular weights and also for other cationic polyelectrolytes. Furthermore, a single curve is obtained for all polyelectrolytes under study when the peak position is plotted vs the monomolar concentration C_p, i.e., the effect is independent of the degree of polymerization. The expelled clear, isotropic, and slightly viscous bottom phase has been quantitatively analyzed using high performance liquid chromatography. It contains $C_{10}E_3$ on the order of one half of its critical micelle concentration, and most of the polymer. The phase separation obviously arises from a competition of the repulsive electrostatic forces between the slightly charged membranes and the osmotic pressure of the excluded polyelectrolyte solution. Increasing the osmotic pressure destabilizes the stack of membranes and squeezes the lamellar phase. The squeezing effect is, in a good approximation, proportional to C_p as it is expected for salt-free polyelectrolyte solutions.

Figure 2 shows a set of light spectra obtained for $\gamma_0 = 3.12$ wt %, and increasing amounts of PDADMAC. After an initial concentration range where no reflection could be observed, a pronounced peak appears around 415 nm which, upon increasing C_p, shifts toward smaller wavelengths and additionally splits into several single peaks, indicating morphologies which are not plainly lamellar. The depicted single spectra of Fig. 2 (except spectrum b) were measured each at the same time (1 h) after stepwisely increasing C_p. The intensity ratio of the single peaks depends markedly on C_p, but the ratios of the peak positions are essentially constant. The inset of Fig. 2 demonstrates the occurrence of long-time
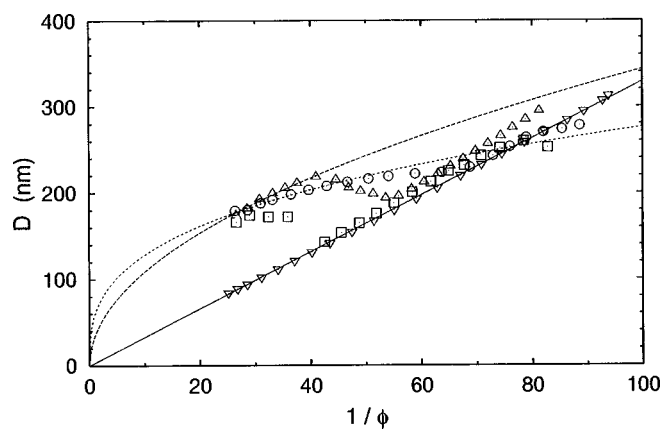
FIG. 4. Characteristic periodic spacing D vs reciprocal surfactant volume fraction $1/\Phi$ for PDADMAC of various molecular weights: $M_n = 3.1 \times 10^4$ ($\square$), 1.62×10^5 ($\triangle$), and 4.5×10^5 ($\bigcirc$); polymer-free sample ($\triangledown$). The surfactant molecular volume used to calculate Φ is 0.515 nm^3. The lines are fits to linear (solid line, $\triangledown$), quadratic (dashed line, $\triangle$), and cubic (dotted line, $\bigcirc$) swelling laws. The prefactor in the linear case is 3.26 nm (effective bilayer thickness).
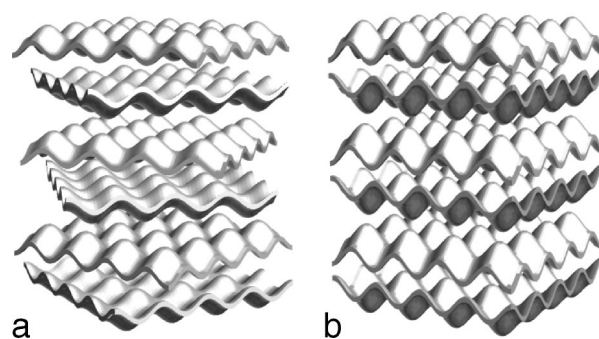

FIG. 5. Structure models for the deformed surfactant bilayers after polyelectrolyte addition: Quadratically undulated lamellar bilayers, stacked (a) in a rotationally disordered way, and (b) in an ordered A-B sequence.

structural rearrangements. A spectrum like b was also measured for $M_n = 4.5 \times 10^5$ already after 1 h.

The characteristic periodic spacing of the structure for both surfactant concentrations has been calculated from $D = 2\pi/Q_0$, where Q_0 is the position of the first peak in wave vector space ($Q = 4\pi n \lambda^{-1} \sin \theta/2$; n is the refractive index of the solution, and θ the scattering angle), and is plotted vs C_p in Fig. 3.

The most remarkable feature is the behavior of the more concentrated system. The appearing reflection corresponds to a much higher spacing D as compared with the theoretically expected value. This effect could easily be understood by phase separation. However, the solutions were birefringent, only slightly cloudy, and no macroscopic phase separation could be observed during a period of at least six weeks. Therefore, we suppose a structure which gathers considerably more surfactant in the interface compared to the L_α phase. At that wavelength where we expected the Bragg peak of the L_α phase, corresponding to the initial surfactant concentration γ_0 ($\lambda_{max} = 265$ nm), the samples are extremely clear and show the typical lamellar reflection. For even larger C_p the sample become turbid again, while the spectra resemble those with a low surfactant concentration after phase separation. Excluding phase separation as a possible explanation for the decreasing spacing D at low C_p it must be considered that increasing C_p results in higher amounts of incorporated polyelectrolyte. Increasing electrostatic screening could lead to smaller radii of gyration and a reduction of the polyelectrolyte-induced intermembrane interaction. The critical surfactant concentration where the nonlamellar structure is established depends upon the polymer molecular weight. Hence, for $M_n = 4.5 \times 10^5$ and 3.1×10^4 (contour lengths 1530 and 105 nm), we determine $\gamma_c = 1.55$ and 2.8 wt % (critical spacings 200 and 110 nm), respectively, indicating clearly a chain length effect. Shorter chains need obviously a smaller initial interlamellar spacing to induce the structural modification.

To obtain more information about the structure, swelling

experiments were carried out. In Fig. 4 the characteristic periodic spacing D is plotted vs the reciprocal surfactant volume fraction $1/\Phi$ for three polymer containing samples with different molecular weights. In all samples the fixed molar ratio $[C_{10}E_3]/$[PDADMAC monomers] was about 9×10^2. The measurements started at identical initial surfactant concentrations of $\gamma_0 = 3.5$ wt % after adding PDADMAC. The initial spacing is nearly identical in all cases. After stepwisely diluting the sample with pure water, the represented data points (symbols) are obtained. For comparison the corresponding data of a polymer-free sample (containing 2×10^{-5} M sodium dodecyl sulfate) are added to the figure.

The structure with the shortest polymer chain ($\square$) shows no initial swelling, the one with the medium chain length ($\triangle$) a quadratic swelling law, and the one with the highest M_n ($\bigcirc$) shows a cubic swelling law, corresponding to $D \propto \Phi^{-n}$, with $n = \frac{1}{2}$ and $\frac{1}{3}$, respectively. Upon further dilution the swelling law crosses over to a classical linear one with $n = 1$. The crossover happens the earlier the shorter the polymer chain length is.

Finally, we present arguments in favor of an interpretation of the experimental findings in terms of polymer-bridged structures. Let us look at some of the light spectra from a crystallographic point of view, and discuss possible morphologies. Starting with the equilibrated sample, the scattering curve displayed in Fig. 2, inset b, shows four well-resolved peaks. The ratio of the peak positions is $\sqrt{4}:\sqrt{5}:\sqrt{8}:\sqrt{16}$, at first sight suggesting a cubic structure. However, it is difficult to imagine a cubic morphology, either connected or disconnected, which could be reasonably built up by the present system. Furthermore, a cubic symmetry contradicts the observed birefringence of the sample.

A morphology which can be straightforwardly obtained from the original lamellar system and which is in accordance with the observed scattering curve, is shown in Fig. 5(b). It consists of lamellar bilayers which are quadratically undulated ("egg carton") and stacked in an A-B sequence. The undulation period is equal to the lamellar period, so that the height of the tetragonal unit cell containing two lamellae is twice its base edge. The hkl indexing of the four experimentally observed peaks is (002), (101), (110), and (004). The A-B stacking sequence of the quadratically undulated bilayers leads to a close spatial approach of the undulation

maxima of adjacent lamellae. Bridging should happen at these positions, and is strongly facilitated in the ordered membrane conformation.

The spectrum from the unequilibrated sample (Fig. 2, inset a) shows an interesting extended tail toward the high-Q range. A morphology leading to such a feature in the scattering curve is sketched in Fig. 5(a). While this structure still consists of stacked quadratically undulated lamellar bilayers there is now a lack of orientational correlation from one layer to the next. The scattering consists of (00l) reflections with symmetric and two-dimensional (hk) reflections with a characteristic asymmetric peak shape, respectively [22,23]. Mixed (hkl) reflections are suppressed. The scattering curve shown in Fig. 2, inset a, can very well be resolved into a superposition of such symmetric and asymmetric peaks.

It is known [24] that the kinetics of polyelectrolyte adsorption is slow, and long-time structural rearrangements leading to energetically more favorable polymer conformations normally occur. These could induce the observed changes of membrane superstructure, and support the presented model of membrane undulations originating from bridging by polyelectrolyte chains.

The swelling behavior (Fig. 4) supports the bridging model. The different swelling laws in the initial range suggest M_n-dependent structure formation. In the intermediate range, D decreases, which may be understood by beginning interruption of bridges, flattening of the membranes, and building of new lamellae. When all bridges are interrupted, linear swelling occurs, the onset of which correlates with the chain length in the expected way.

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