Layer Compression Modulus of Electrostatically Stabilized Lyotropic Lamellar Phases Revisited: Application to the Quantitative Analysis of a Polymer Induced Critical SmA–SmA Phase Separation

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Abstract. — We present a calculation of the smectic compression modulus $\overline{B}$ of a lyotropic lamellar phase stabilized by electrostatic interactions. This calculation, based on a numerical solution of the Poisson-Boltzmann equation, shows that the classical analytical expressions of $\overline{B}$ given in the literature in the two asymptotic limits (absence of added salt, or large added salt concentration) are valid under very restrictive conditions only. The motivation of this study lies in the understanding of the physical behavior of a doped amphiphilic lamellar phase formed from a mixture of non ionic surfactants (Triton X100/Triton X35), cationic surfactant (cetylpyridinium chloride), water, decane and water-soluble polymer (polyvynilpyrolidone). A critical lamellar/lamellar phase separation observed in our system is quantitatively well-explained by using both the present calculations and a recent model proposed by Ligoure *et al.* which predicts the polymer-mediated intermembrane interaction contribution to the smectic compression modulus.

1. Introduction

Lyotropic lamellar phase, in which amphiphilic molecules in solution self assemble to form layers that stack with long range periodicity, have been subject of much interest. In particular, much attention has been focused on the understanding of the interactions between these membranes [1]. The basic forces between two parallel membranes separated by a water layer, involve both attractive and repulsive interactions. In the case of neutral bilayers, the dominant repulsive interaction between fluid membranes is the so-called Helfrich's interaction [2]. However, for interlamellar distance below 20 Å, the dominant repulsive interaction is the hydration one [3]. In the case of charged bilayers, another repulsive interaction must be taken into account, which often dominates the other ones; *i.e.*, the electrostatic interaction. Analytical expressions of the electrostatic interaction can be found in the literature in two asymptotic

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limits: absence of added salt or large enough added salt concentration. However, in many practical cases, the situation is intermediate between these two asymptotic regimes, and, as shown by Dubois *et al.* [4], who investigated both experimentally and theoretically the osmotic pressure of charged lyotropic smectics, these analytical expressions fail.

The most well-known attractive interaction is the long range van der Waals interaction between membranes [5,6]. However, it is often negligible in unbinding lamellar systems [7]. One way to induce strong attractive interactions between adjacent bilayers is to incorporate a guest component in the solvent of the lamellar phase [8–12]. For instance, it has been shown experimentally that addition of a water-soluble neutral polymer in lamellar phases induces a softening of the smectic order [8,9], as predicted theoretically [8].

One of the most important thermodynamical characteristics of the smectic phase is the layer compression modulus $\overline{B}$ which is directly related to the interaction energy between membranes [8]: the case of a critical lamellar/lamellar phase separation is of particular interest, because at such a critical point $\overline{B}$ must vanish. The techniques used to measure $\overline{B}$ (elastic properties of lyotropic lamellar phase) include high-resolution X-ray scattering [1,8], dynamic light scattering [13] and surface force apparatus [14]. The experimental system we have investigated consists mainly of a charged lamellar phase, whose surface area per charged head Σ of the membrane can be modified by doping the initially neutral bilayers with a controlled amount of ionic surfactants. In this system, we have added a water-soluble polymer which is distributed into the aqueous solvent only. In this case, the two dominant interactions are the electrostatic one (repulsive) and the polymer-mediated one (attractive). At a fixed appropriate amount of polymer, a critical L_α/L_α phase separation is encountered by increasing the surface area per charged head. Note that the experimental conditions are such that we are far from both asymptotic electrostatic regimes discussed above. Using our present calculation, for the electrostatic contribution to the layer compression modulus as well as the polymer contribution to $\overline{B}$ calculated in reference [8], it is possible to explain quantitatively the existence of this critical point: the total layer compression modulus vanishes at the critical experimental conditions. The paper is organized as follows. In Section 2, we present a general calculation of the layer compression modulus of any charged lamellar phase, based on the numerical resolution of the Poisson-Boltzmann equation, as done in references [4,15,16]. Particular attention will be paid to show the very limited range of validity of the analytical expressions of $\overline{B}$. In Section 3, we examine the critical point and the phase separation into a polymer-rich and a surfactant-rich lamellar phase occurring upon progressive subtraction of ionic surfactant at suitable polymer concentration, in the experimental system we have investigated. The results of the previous section for the electrostatic contribution and some recent ones for the polymer contribution [8] are used in order to calculate the total compression modulus. Their balance at the critical conditions meets nicely the experimental observation.

2. General Calculation of the Smectic Compression Modulus of an Electrostatically Stabilized Lamellar Phase

In a lyotropic smectic phase, two successive lamellae of thickness δ are assumed to be perfect planar charged surfaces separated by a water (or brine) layer of thickness $d_w = 2d$. Each plane carries a charge density $\sigma = 1/\Sigma$ where Σ is the surface area per charged head of the membrane, c_s denotes the mean salt concentration of the solvent. In order to obtain the interaction energy between two adjacent membranes, one needs to solve the classical non linear differential Poisson-Boltzmann equation, with appropriate boundaries and conservation conditions [4]. One elegant and powerful method to do that is to use a grand canonical approach, *i.e.*, to imagine that the lamellar phase is in contact with a reservoir at a fixed

but unknown salt concentration c'_s, so that the free ions in the reservoir and in the lamellar phase are in thermodynamical equilibrium. Details can be found in reference [4]. Under these conditions the Poisson-Boltzmann equation becomes [4]:

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} = K'^2\sinh(\Phi(x)) \tag{1}$$

with the following boundaries and conservation conditions:

$$\left(\frac{\mathrm{d}\Phi}{\mathrm{d}x}\right)_{x=d} = 0 \tag{2a}$$

$$\frac{\mathrm{d}\Phi(0)}{\mathrm{d}x} = -4\pi l_B\Sigma \tag{2b}$$

$$c_s = c'_s\frac{1}{d}\int_0^d \exp[-\Phi(x)]\mathrm{d}x \tag{2c}$$

where $K' = (8\pi l_B c'_s)^{1/2}$, and $\Phi = e\Psi/kT$, $\Psi(x)$ is the electrostatic potential at a distance x from one of the surface ($0 < x < d$). $l_B = e^2/(4\pi\epsilon kT) = 7.2$ Å is the Bjerrum length at room temperature. For check of simplicity we have considered a ionic monovalent salt, as NaCl for instance and assumed that the membranes are positively charged. Equation (2c) relates the mean salinity c_s to the salinity in the reservoir and expresses the global electric neutrality of the lamellar phase. Since $\Phi(x)$ is positive everywhere, the salinity c_s is lower than the salinity c'_s in the reservoir. This salt exclusion is called the Donnan effect [4], and is amplified as the interlamellar distance is decreased or as the surface area per charged head is increased. It has been experimentally observed by direct measurements of the ionic concentration in the lamellar phase [17].

The osmotic pressure is then easily obtained [4]:

$$\Pi = 4kTc'_s\sinh^2\left(\frac{\Phi(d)}{2}\right). \tag{3}$$

The free energy per unit area can be deduced from this expression [1]:

$$f_{\mathrm{elec}} = -\frac{1}{2A}\int_v \Pi\delta v = -\frac{1}{2}\int_\infty^{d_w} \Pi(d)\,\delta d \tag{4}$$

where A is the area of a plate and $\delta v = A\delta d$.

Assuming now, that the membranes are incompressible, i.e., δ constant, this assumption is in fact not very restrictive: many experimental reports have shown that the bilayer thickness of most lyotropic smectics remains constant along a broad dilution range [1,18] and the layer compression modulus simply writes [8]:

$$\overline{B} = d_p\frac{\partial^2 f}{\partial d_p^2} \tag{5}$$

where $d_p = d_w + \delta$ is the smectic periodicity. From equations (4) and (5), one obtains the following general expression for $\overline{B}$:

$$\overline{B} = -kTd_p c'_s\sinh(\Phi(d))\frac{\partial\Phi(d)}{\partial d_p} \tag{6}$$

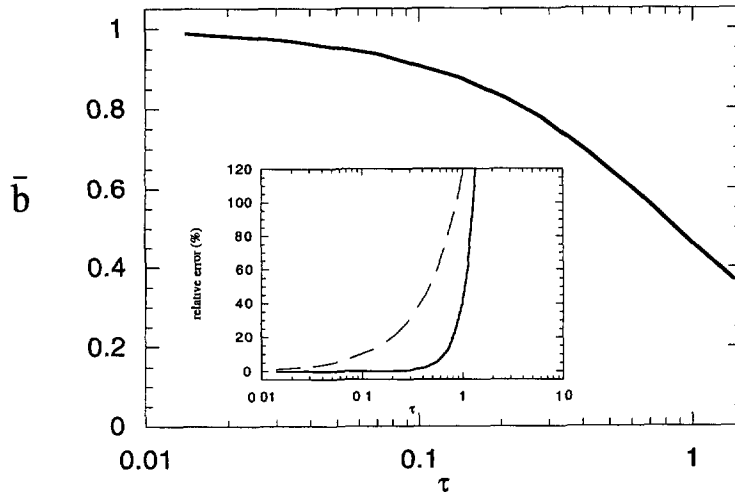where the first derivative is calculated at constant membrane thickness.

Fig. 1. — Variation of the layer compressional modulus in reduced units $\bar{b}$ *versus* the reduced surface area per charge of the membrane τ ($\tau = \Sigma/(d_w l_B)$): master curve $\bar{b}$ vs. τ. Inset: the relative error $(\bar{b}_{an} - \bar{b}_{num})/\bar{b}_{num}$ is plotted as a function of τ where $\bar{b}_{an}$ is given by equation (7), and $\bar{b}_{num}$ by the numerical calculation. The dotted line (respectively solid line) represents the first term (respectively the three first terms) of equation (7).

Now we have solved numerically equation (1), with boundaries conditions given by equations (2a–c), using the iterative procedure detailed in Appendix B of reference [4]. Note that Monte-Carlo simulations taking into account the ionic correlations have checked the success of the Poisson-Boltzmann approach [4]. From this numerical integration of the Poisson-Boltzmann equation, and using equation (6), one can calculate the electrostatic layer compression modulus $\overline{B}$ as a function of the physical parameters of the lamellar phase, *i.e.*, d, Σ and c_s. We can now compare the numerical values of $\overline{B}$ we have obtained with the analytical expressions given by the literature [1, 19] in the two asymptotic regimes discussed above.

2.1. NO SALT ADDED. — In this case $c_s = 0$ [20], and one can define the layer compression modulus in reduced units: $\bar{b} = \dfrac{2 l_B d_w^3}{\pi k T d_p} \overline{B}$ which depends only on the dimensionless parameter $\tau = \Sigma/(d_w l_B)$. Figure 1 shows the variation of $\bar{b}$ as a function of τ (master curve), obtained from our numerical procedure. Note that this curve is *universal, i.e, valid for any electrostatically stabilized lamellar phase in the absence of added salt*. We can now compare this "exact value" to the analytical expression given in the literature [1], in the limit where $\tau \ll 1$:

$$\bar{b}_{an} = 1 - 3\tau + 6\tau^2 + \cdot \tag{7}$$

In the inset of Figure 1 the relative difference $(\bar{b}_{an} - \bar{b}_{num})/\bar{b}_{num}$ is plotted as a function of τ, where $\bar{b}_{an}$ is given by the first term or the three first terms of the right handside of equation (7) and $\bar{b}_{num}$ is calculated using the numerical procedure developed above. First of all, the analytical expressions overestimate $\bar{b}$ in all cases. Secondly, the use of the first term only of the series (7) leads to a very rough estimation of $\bar{b}$. Thirdly, down to a value $\tau = 0.55$, the relative error made by using the analytical expression (7), is less than 5%; however, above this value, the error increases dramatically, and the analytical expression $\bar{b}_{an}$ must be rejected.
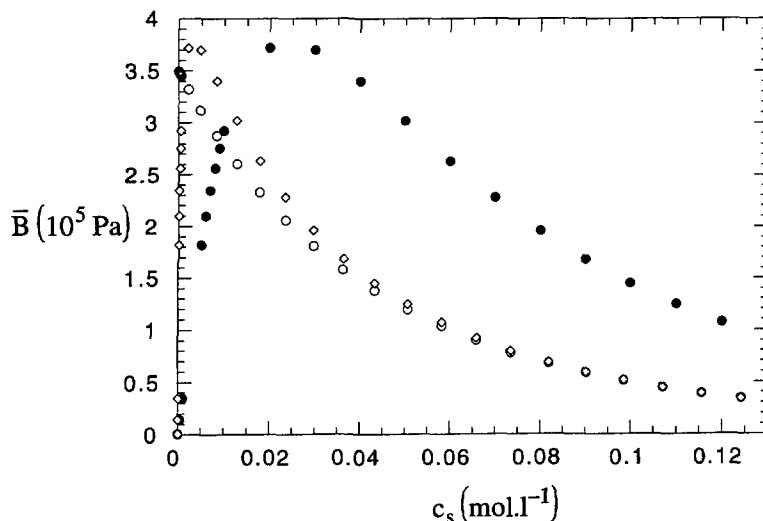
Fig. 2. — Comparison between numerical calculation and asymptotic analytical expressions of $\overline{B}$ versus the salt concentration c_s in the solution: (o) numerical calculation; (•) weak overlap approximation; (◊) Weak overlap approximation with Donnan effect.

2.2. WEAK OVERLAP APPROXIMATION. — In this case the electrostatic interaction is screened by the presence of a sufficiently large amount of salt in the solvent. Using the weak overlap approximation [19], the layer compression modulus becomes:

$$\overline{B} = \frac{4kT d_{\mathrm{p}}}{\pi \lambda_{\mathrm{D}}^3 l_{\mathrm{B}}} \gamma^2 e^{-d_{\mathrm{w}}/\lambda} \tag{8}$$

where $\gamma = \tanh\left[\frac{1}{2}\mathrm{arcsinh}\left(2\pi\frac{l_{\mathrm{B}}\lambda}{\Sigma}\right)\right]$, $\lambda(\text{Å}) = \dfrac{3.04}{\sqrt{[c_s]}}$ is the Debye length (c_s is expressed in mol/l). This expression is valid under the condition $d_{\mathrm{w}}/\lambda \gg 1$. As pointed out by Dubois et al. [4], this expression is in fact not correct, however, it remains valid, if the salinity of the solvent c_s is replaced by the salinity c'_s of the fictious reservoir in contact with the lamellar phase. This is a consequence of the Donnan effect: the difference between the two salinities is not exponentially small but is appreciable, even at large d_{w}. Under the condition $d_{\mathrm{w}}/\lambda \gg 1$, there is a simple relation between c_s and c'_s: $c_s \cong c'_s\left(1 - 4\frac{\lambda'}{d_{\mathrm{w}}}\right)$ where λ' is the Debye length of the reservoir [4]. Figure 2 shows the variation of $\overline{B}$ as a function of the mean salinity c_s for a given layer thickness $d_{\mathrm{w}} = 50$ Å and a given charge density $\sigma = 5 \times 10^{-3}$ Å^{-2}. The "exact" calculation based on the use of equation (6) and the numerical resolution of the Poisson-Boltzmann equation is compared with the two approaches that yield analytic expressions for $\overline{B}$: the first one is simply equation (8), where the Donnan effect is neglected, and the second one is obtained semi numerically, from equation (8), but replacing c_s by c'_s (the relation between the two salinities is obtained from the numerical resolution of Eq. (2c)). Obviously expression (8) which neglects the Donnan effect in the weak overlap approximation is not correct and overestimates strongly the layer compression modulus. On the contrary, the weak overlap approximation taking into account the Donnan effect seems a good approximation in this case. However, in our experimental system, $\Sigma > 200$ Å^2, $d_{\mathrm{w}} = 33.5$ Å and $c_s = 7 \times 10^{-3}$ mol l^{-1}, both expressions for $\overline{B}$ are not correct, and one has to use our numerical procedure.

The importance of the Donnan effect is crucial as shown in reference [8], in order to obtain a quantitative of $\overline{B}$, in particularly when the electrostatic interaction compete with another one of the same order of magnitude.

3. Experimental

Our experimental system consists of lamellar phases obtained from a ternary mixture of two non-ionic commercial surfactants Triton X100 (TX100) and Triton X35 (TX35) and water. The weight ratios: TX100/TX35 = 55/45 g/g and (TX100 + TX35)/H$_2$O = 1 g/g are kept constant in all samples. Decane has been incorporated in order to fluidity the solution and to obtain a much better contrast in Small Angle X-ray Scattering experiments, it inserts between tails of surfactants, increasing the bilayer thickness [21].

The membrane is then "doped" by a cationic surfactant, cetylpyridinium chloride (CPCl), by adding a small variable amount of this surfactant into the samples in order to obtain an electrostatically stabilized smectic with a controlled surface area per charged head Σ. It has been shown that CPCl is entirely dissociated in water [22], so that the previous PB theory can be applied without introducing any effective charge due to the binding of counterions on the bilayer surface [23]. In such a way, one can increase the repulsive electrostatic interaction between membranes by adding more CPCl. In this doped system, we also have incorporated a water-soluble neutral polymer polyvynilpyrolidone (PVP). The reported number average molecular weight is 10 000. It has been experimentally proved [8] that PVP does not affect the bilayers of a lyotropic smectic made from CPCl, hexanol and water or brine, i.e., the polymer is distributed into the aqueous solvent only and leaves the membrane thickness constant. Our experimental results are consistent with this picture. More experimental details on this system will be discussed in a forthcoming publication [21].

We focus here on a particular series of samples where the total weight ratio of decane is constant (0.13 g/g) and the volume fraction of polymer in water $\overline{\Phi}$ is also constant (0.14 g/g). The water layers are then in fact a three-dimensional, semi-dilute solution of PVP as discussed in reference [8]. The total volume fraction of surfactant (TX100 + TX35 + CPCL) is fixed, but we progressively increase the surface area per charged head Σ, by replacing progressively the ionic surfactant by the non ionic ones (note that during this process the weight ratio TX100/TX35 = 55/45 g/g is preserved). In Figures 3 are represented the X-ray scattering patterns of this series of samples. In the range 150 Å^2 < Σ < 265 Å^2, the samples are monophasic, birefringent. The X-ray patterns reveal a lamellar structure with a smectic periodicity $d_{\mathrm{p}} = 80 \pm 1$ Å. Note however, the broadening of the first peak, which indicates that, increasing Σ weakens the effective interlayer interaction. At $\Sigma = 320$ Å^2, the sample becomes cloudy and we observe strong scattering at small angle and broadening of the peak. The Bragg peak splits in two separates peaks which reveal the presence of two coexisting lamellar phases, of very close periodicities. At still higher Σ, the maxima separate more and more and progressively sharpen. So, finally, one of the peaks (corresponding to the larger smectic periodicity) disappears and is replaced by a bump, i.e., one isotropic phase coexists with a lamellar one. These experimental observations prove that the lamellar/lamellar phase separation which is observed around $\Sigma = 320$ Å^2 corresponds to a critical point or is very close to a critical point [11]. We can compare this transition to that one described in reference [8]. In both cases a critical lamellar/lamellar phase separation is observed, by reducing the repulsive electrostatic interaction between the membranes, in the presence of polymer only. However, in the present case this is done by decreasing the surface charge density of the membranes, whereas it is done by increasing the salt concentration in the solvent in the other case.
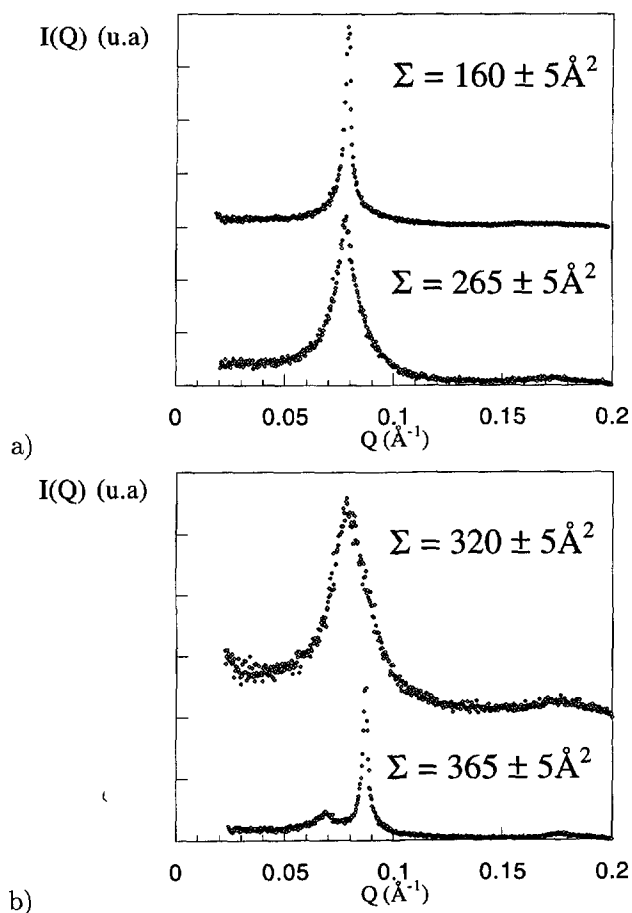
Fig. 3. — Small Angle X-ray Scattering patterns of a series of samples at constant volume fraction of the membrane $\Phi_m = 0.57$ and constant volume fraction of polymer in the solvent $\overline{\Phi} = 0.14$. The only variable parameter is the surface area per charge head of the membrane Σ. A critical lamellar/lamellar phase separation occurs for $\Sigma = 320$ Å^2.

4. Discussion

We have observed experimentally a critical L_α/L_α phase separation, for which the *total layer compression modulus* $\overline{B}_{tot}$ *must vanish*. In our system, the two dominant interactions are the repulsive electrostatic interaction which has been discussed in detail in the preceding section, and the attractive polymer-mediated interaction. One can evaluate other interactions such as hydration and van der Waals and see that they are negligible [1,8]. The non classical attractive polymer-mediated interaction has been recently theoretically discussed [8,24]. This contribution to the layer compression modulus has been analyzed in reference [8]. It is always negative, but its analytical expression depends on the regime of confinement of the macromolecular solution sequestered in between the membranes. In our experimental case, the confinement regime is that of a three-dimensional semi-dilute solution. In this case, the polymer *contribution to*
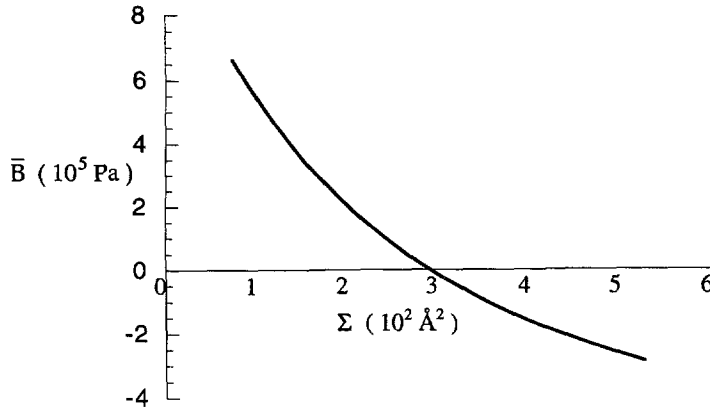
Fig. 4. — Variation of the theoretical total layer compression modulus as a function of the surface area per charge of membrane corresponding to the series of samples of Figure 3. $\overline{B}$ vanishes for $\Sigma = 300$ Å^2 which corresponds to the critical L_α/L_α phase separation observed in Figure 3.

the layer compression modulus becomes [8]:

$$\overline{B}_{\text{pol}} = -d_{\text{p}} \frac{kT 9\rho^2 \overline{\Phi}}{ad_{\text{w}}^3 \left(\dfrac{45\beta\overline{\Phi}^{1/4}}{16} + \dfrac{3\rho a \overline{\Phi}^{-1/2}}{2d_{\text{w}}} \right)} \tag{9}$$

where a is the persistence length of the polymer, d_{w} the water layer thickness and $\overline{\Phi}$ the volume fraction of polymer in water. $\beta \approx 1.97$ and $\rho \approx 0.985$ are universal prefactors calculated in reference [24]. A reasonable hypothesis is to suppose that the polymer-mediated and electrostatic interactions are not coupled. In this case the total layer compression modulus becomes:

$$\overline{B}_{\text{tot}} = \overline{B}_{\text{elec}} + \overline{B}_{\text{pol}} \tag{10}$$

where $\overline{B}_{\text{elec}}$ can be calculated numerically from equation (6) and $\overline{B}_{\text{pol}}$ is given by equation (9). The total layer compression modulus $\overline{B}_{\text{tot}}$ (Eq. (10)) corresponding to the above experimental series is plotted in Figure 4 as a function of Σ, the surface area per charged head of the membrane area, using the following experimental values: $d_{\text{w}} = 33.5$ Å (according to the X-Ray spectrum), $a = 4$ Å, $\overline{\Phi} = 0.14$ and $c_{\text{s}} = 7 \times 10^{-3}$ mol l^{-1} This weak salinity is due to the presence of ionic impurities in Triton X, which are commercial products, used as received, and is obtained from standard conductivity measurements. Note that the polymer contribution $\overline{B}_{\text{pol}}$ is constant, since the volume fraction of polymer as well as the layer thickness are kept constant in this series of samples. One finds numerically that $\overline{B}_{\text{tot}}$ vanishes for $\Sigma = 300$ Å^2 (see Fig. 4). Note that there is no adjustable parameter. This theoretical result agrees remarkably well with the observed critical point occurring close to $\Sigma = 320$ Å^2 (see Fig. 3). Note that the use of the asymptotic approach values of $\overline{B}_{\text{elec}}$ discussed in the preceding section, rather the "exact" one calculated in the present paper, would lead to a wrong prediction for the critical value of Σ. This bears out the numerical procedure described in this paper. Finally this result seems also to confirm the theoretical calculations of the polymer-mediated contribution to the smectic compression modulus proposed in reference [8]. Others critical points [21] have been observed in our experimental system and can be explained using the same approach.

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