

Colloid Science

Extreme swelling of a lyotropic lamellar liquid crystal

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Abstract: The evolution of the OBS/water/decane/pentanol lyotropic lamellar crystal is followed from 0% to more than 90% decane content. The lamellar spacing (d) varies then from 35 Å to 11 000 Å. The swelling is followed with small angle x-ray scattering and the Bragg divergence in the intensity is found to disappear in moderately swollen lamellar crystal (d from 200 Å up to 800 Å) while the central scattering increases. More striking is the reappearance of the Bragg divergences observed by SAXS (d from 800 Å to 1100 Å) and for extremely swollen lamellar crystals in the angular distribution of scattered light (d from 2 000 Å to 10 000 Å). We discuss these observations along the lines of the recent models of swollen lamellar liquid crystals and in particular the apparent evolution of the dilute lamellae.

Key words: Lyotropic-lamellar-liquid-crystal, dilution, SAXS, light-scattering.

Introduction

Lyotropic lamellar liquid crystals (LLC) are found in a number of systems containing surfactant molecules. They consist of hydrophilic and hydrophobic layers alternatively and regularly packed, and thus exhibit a smectic periodicity. The average periodicity of these LLC phases is found to vary over a wide range with composition. A number of examples are found where an LLC with initially symmetrical hydrophilic and hydrophobic parts can be swollen by water (or brine) [1–5] or by oil [6–9]. In the resulting phase thin hydrophobic/hydrophilic layers are separated by thick water/oil layers. It is important to note that, even at the highest dilutions, these phases exhibit an important birefringence characteristic of a long-range orientational order. The evidence of a quasi long-range positional order has been obtained in a number of cases through the observation of a Bragg singularity [10] in the small angle x-ray scattering (SAXS). These phases have attracted a lot of interest recently because they offer an unique opportunity to study the interactions between lamellae (thickness \approx some tens Å) over a large range of distances. The usual interactions encountered in colloids namely: van der Waals attrac-

tion, generally repulsive screened electrostatic and hydration forces [11] are effective over distances less than \approx 100 Å while much larger repeat distances have been observed in LLC. To explain the stability of these swollen phases Helfrich [12] postulated a long-range steric interaction arising from the thermally induced out-of-plane fluctuations of the lamellae. Experimental evidence of the role of this long-range interaction in the swollen lamellar phases was obtained by a quantitative study of the profile of the Bragg singularity in oil swollen [8] or brine swollen [4] LLC., while the possible competition between this long-range steric interaction and the long-range electrostatic interaction was studied recently in a water or brine swollen LLC [5].

The ternary system OBS/water/pentanol (OBS = *n*-octylbenzenesulfonate) has been extensively studied in our group [13]. The dilution with decane of the lamellar liquid crystal (LLC) of this system was investigated and it was shown that a dilution with constant lamellae (unidimensional expansion) was possible, providing the diluant was a mixture, in the right proportions, of decane and pentanol [14]. More recently, we showed that it was possible to pursue the dilution up to an extremely swollen lamellar phase [7] amen-

able to a study by light diffraction. We report here on a systematic study of the swelling and extreme swelling of this LLC by a mixture of decane and pentanol in the quaternary system sodium *n*-octylbenzenesulfonate/water/pentanol/decane. All experimental evidences confirm the previous conclusion [14] that moderate dilution results in swelling of the initial ternary LLC with constant lamellae. The evolution of the small angle x-ray scattering (SAXS) pattern is then analogous to that observed for other systems [15]. We also confirm that it is possible to dilute the LLC up to more than 99% diluent, thus obtaining an extremely swollen LLC, but at these larger dilutions the experimental evidences lead to a puzzle. The smectic order becomes harder as is manifest from the observation of two and even three Bragg singularities in the light-scattering pattern; the interaction responsible for this hardening of the lamellar stacking is still in question. Furthermore the lamellae composition, as well as the apparent thickness (which can be deduced from the data), also points to a definite rupture of the properties of the LLC when going from the dilute to the extremely dilute regime.

Experimental

Sample preparation

Sodium *n*-octylbenzene sulfonate is synthesized [16] and purified as described in [13]. 1-pentanol (Merck p.a.) and decane (Fluka purum) are used as received and water is triply distilled. The samples are prepared by weight, as described below, and the corresponding volume fractions are calculated using the densities given in [14].

From a very partial exploration of the phase diagram of the quaternary system we found that the domain of existence of the LLC has the features depicted very schematically on Fig. 1; they imply that the same diluent cannot be used all the way from the ternary system up to the extremely dilute LLC and that the proportions of water/pentanol/OBS vary over a very narrow range in the phase domain of the extremely swollen lamellar crystal. Too much OBS leads to the apparition of crystallites. An increase in pentanol leads to an isotropic phase. A small increase in water leads to the apparition of a phase analogous to the anomalous isotropic phase observed near to the swollen lamellar phase in water-rich systems, namely a flow birefringent phase [17]. With a further increase in water an isotropic, transparent phase is observed. Because of these features of the phase diagram we had to find a very stringent procedure of sample preparation in order to follow the swelling of the lamellar liquid crystal up to extreme dilution.

A first set of samples (I) was prepared by dilution of a ternary LLC with a mixture of decane and pentanol in the ratio 9:1. The last sample of the set (I) had a lamellar spacing of about 1100 Å; and its further swelling by dilution with the same diluent was impossible. Two other sets (II) and (III) were prepared by dilution of two swollen samples ($d \approx 1100$ Å) with hyperswollen samples

($d \approx 10\,000$ Å and $d \approx 11\,000$ Å). This procedure was found to be the safest in order to dilute with the appropriate diluent.

Experimental procedures

All samples are observed to be birefringent: an evidence of the persistence of a long-range orientational order and to display, under appropriate conditions, focal conics and oily streaks characteristic of a lamellar structure.

The samples to be studied by SAXS are filled into cylindrical Lindeman glass capillaries (diameter = 1,5 mm). The samples to be studied by light scattering are filled into cylindrical glass cells (diameter = 12 mm). Except for the less diluted LLC (pitch from 35 Å to c.a. 200 Å) which yielded powdered samples, the lamellae achieved, after a certain time, a cylindrically symmetric configuration (cf. [4]). This configuration is checked by polarized light microscopy or between crossed nicols.

Most SAXS measurements have been performed on our laboratory set-up. It usually works in linear collimation, here the incident and diffracted beams are diaphragmated in order to simulate properly a punctual configuration. For moderately swollen samples (pitch from 200 Å upward) SAXS have been performed on line D 22 at the synchrotron light source in LURE: the collimation is truly punctual.

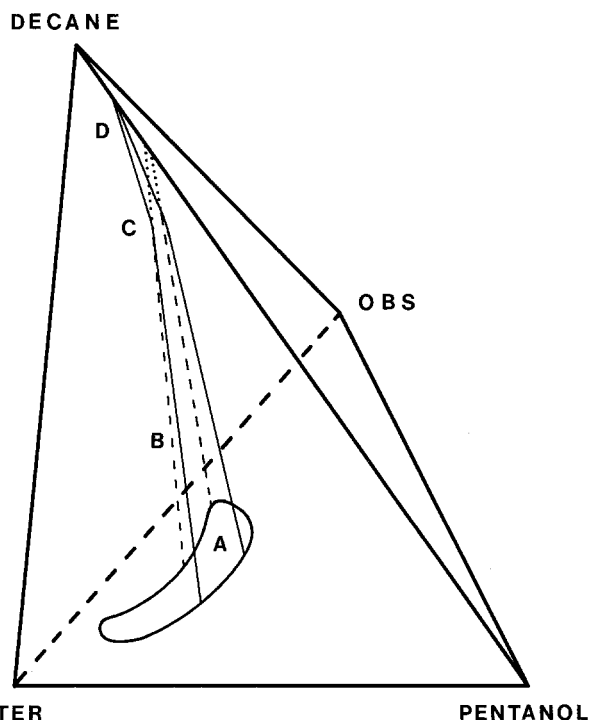


Fig. 1. Schematic of the domain of existence of the lamellar liquid crystal in the quaternary system OBS/water/pentanol/decane. A: LLC in the ternary system OBS/water/pentanol; B: the swollen LLC (dilute regime). C: region of transition between B and D; D: the hyperswollen LLC (extremely dilute regime)

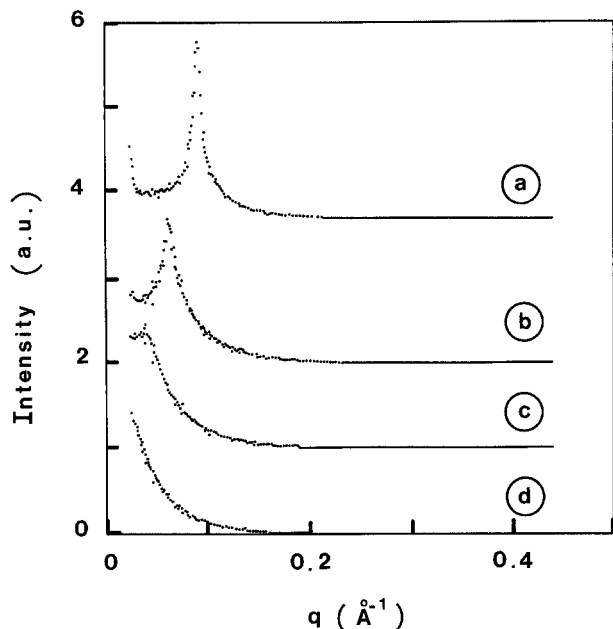


Fig. 2. SAXS pattern for four swollen samples with the decane volume fraction equals to a): 45% $d = 70$ \AA , b): 59% $d = 100$ \AA , c): 69% $d = 150$ \AA , d): 75% expected $d \approx 200$ \AA . Note the increase of the central scattering when going from a) to d), and the total disappearance of the Bragg singularity in d)

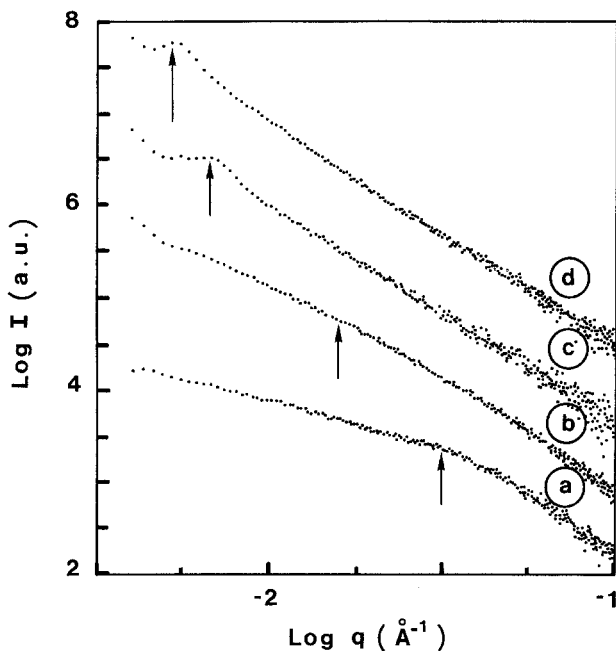


Fig. 3. SAXS pattern for four swollen samples with the decane volume fraction equals to a): 75% expected $d = 200$ \AA , b): 82.5% expected $d \approx 400$ \AA , c): 86.5% $d \approx 900$ \AA , d): 87.3% $d \approx 1100$ \AA . The log-log plot is chosen for clarity. Note the important central scattering and the absence of any trace of Bragg singularity in a) and b), while it reappears faintly in c) and d). (Its position or expected position is indicated by an arrow)

The light scattering experiments have been performed on the laboratory set up: the light source is an argon ion laser working at 4880 \AA , the beam is focalized on the sample and the scattered light is collected as a function of scattering angle on a photomultiplier.

In the three experiments the cylindrical axis of the sample is perpendicular to the scattering plane so that a substantial part of the scattering volume is illuminated according to the Bragg condition. The resolution on the scattering vector is of the order of a percent.

Results and discussion

The obtained scattering patterns are shown in Figs. 2 to 4. For the most concentrated samples the pattern displays a clear Bragg singularity as shown in Fig. 2. From the position of this singularity, the periodicity (d) of the sample can be deduced. The central scattering can be seen to become increasingly important with

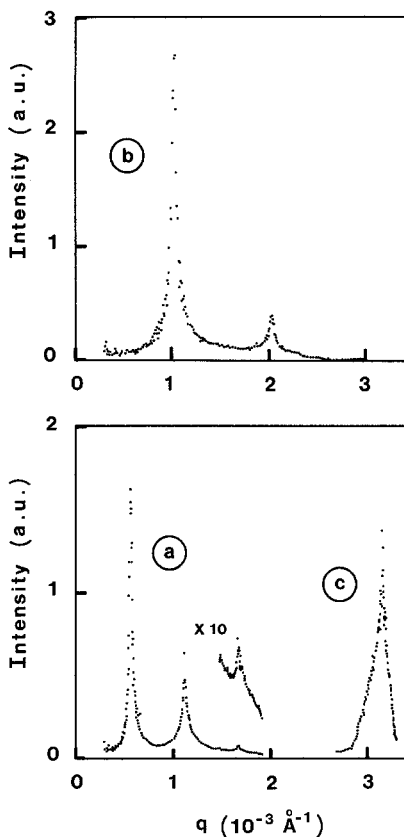


Fig. 4. Light-scattering pattern for some extremely swollen samples. Note the absence of central scattering, the sharpness of the first order singularity, and the existence of the second and even third order singularities in the most swollen samples. Φ_{decane} and d are, respectively: a) 89.3%, 10 400 \AA , b) 91.9%, 6 000 \AA , c) 92.4%, 2 000 \AA

dilution and to be the only scattering from the sample for which the periodicity is expected to be around 200 Å (by continuity from the composition): that is the Bragg singularity has altogether disappeared. In order to test that this disappearance was real and not an experimental artefact, the scattering patterns for samples with expected $d = 200$ Å (powdered) and $d = 400$ Å (oriented) have been measured on D22 in LURE (where larger repeat distances are measurable). They are shown in Fig. 2 on a log-log display: no Bragg singularity is perceptible but an important central scattering is also observed. In Fig. 3, the pattern for more diluted samples (oriented) ($d \approx 900$ Å and $d \approx 1100$ Å) is also shown, although the central scattering remains important; a faint Bragg singularity can be seen to reappear at roughly the expected position.

The very diluted samples were investigated using light scattering and some scattering patterns are displayed in Fig. 4. One notes already for the $d \approx 2000$ Å sample a sharp Bragg singularity. For these highly swollen samples the central scattering has altogether disappeared and not only one, but two and even three singularities are noticeable. Their positions, in the ratio 1:2:3, are in agreement with the postulated quasi long-range positional order of a lamellar phase.

Are the experimental observations compatible with a unique unidimensional expansion of the LLC from the LLC with a periodicity of 35 Å to the LLC with a periodicity of over 10 000 Å? The features of the phase diagram (Fig. 1) already point to a negative answer which is further confirmed by the analysis of the data described below. The second question is then: does the swelling occur with constant lamellae in the dilute regime and with constant but somewhat different lamellae in the extremely dilute regime? If this is the case we can make the following hypotheses in each domain:

1) the lamella is made up of all the OBS plus a part of the pentanol and almost all the water in constant proportions;

2) the diluent contains all the decane plus a part of the pentanol plus, possibly, a small amount of water in constant proportions;

3) the volumes are conserved and this implies that:

$$\frac{d_o}{d} = \Phi_{\text{lamellae}} = (1 - \Phi_{\text{diluent}}) \quad (1)$$

with d_o being the thickness of the lamella, d the periodicity of the lamellar stack, Φ_{lamellae} and Φ_{diluent} the volume fractions of the lamellae and of the diluent.

With these hypotheses we can first take into account the sample's composition alone and write

$$V_{\text{pentanol}} = aV_{\text{OBS}} + cV_{\text{decane}}$$

$$V_{\text{water}} = bV_{\text{OBS}} + dV_{\text{decane}}$$

Where the V s are the volume of the constituents in a sample and the constants a , b and c , d characterize, respectively, the composition of the lamellae and of the diluent. From the composition of any pair of samples belonging to the same domain the corresponding a , b and c , d can be computed. We do obtain an excellent constancy of the values computed from the composition of all pairs within a set. Furthermore, these values are distinctly different for the dilute set I and for the sets II and III. The composition of the lamellae and of the diluent can easily be derived from these constants and are given in Table 1. Although somewhat different values are obtained for the sets II and III, the differences are much smaller than with those of set I, while the high dilution leads to more uncertainties on the composition so that it seems reasonable to assume that the mean values between sets II and III correspond to the extremely dilute regime.

We can also use for each sample both the composition and the pitch d of the lamellar stackings as deduced from the position of the Bragg singularity ($d = 2\pi/q_b$); we then plot the inverse of the d s vs the volume fraction of decane as shown in Fig. 5 for the dilute set I, and in Fig. 6 for the extremely dilute sets II and III. With the above hypothesis and relation (1) we expect a linear plot which yields both the inverse of d_o , and the decane and pentanol proportions for the diluent (assuming negligible water content in the diluent).

As can be seen in Figs. 5 and 6, the plots are indeed linear within one set and here again because of the uncertainties on the composition the slight difference between set II and III will be overseen. The lamella thickness d_o and the diluent composition derived from these plots are given in Table 1.

The results thus confirm that the LLC properties are different in the dilute and in the extremely dilute regimes.

In the dilute regime the above analysis confirms that, upon dilution with the appropriate diluent, the LLC swells with constant lamellae as previously shown [14]. The dilute LLC is a well-behaved lamellar crystal and the interaction responsible for its stability is thus most probably the steric interaction initially suggested by Helfrich [12]. The evolution of the SAXS

Table 1. Lamellae and diluent compositions, and lamellae apparent thickness d_o (b)

Set	d_o (Å)	Lamellae OBS	pentanol	water	diluent decane	pentanol	water
I (a)	Volume Fract (%)	32 ± 0.5	23 ± 0.5	45 ± 0.5	90.5 ± 0.5	9.5 ± 0.5	0
	d_o	35 ± 5			90 ± 0.5	10 ± 0.5	
	n/n_{OBS}	1	1.5 ± 0.5	18 ± 2	—	—	—
II (a)	Volume Fract (%)	19 ± 2	56 ± 5	25 ± 5	93 ± 1	7 ± 1	0.1 ± 0.1
	d_o	75 ± 20			93 ± 0.5	7 ± 0.5	
	n/n_{OBS}	1	7 ± 2	17 ± 2	—	—	—
III (a)	Volume Fract (%)	15 ± 2	67 ± 2	18 ± 2	93.3 ± 0.5	6.6 ± 0.5	0.1 ± 0.5
	d_o	100 ± 20			93.3 ± 0.5	6.7 ± 0.5	
	n/n_{OBS}	1	10 ± 2	15 ± 2	—	—	—
mean values for II + III	Volume Fract (%)	17 ± 2	60 ± 5	22 ± 5	93 ± 1	7 ± 1	0
	d_o	80 ± 20			93 ± 0.5	7 ± 0.5	
	n/n_{OBS}	11	8 ± 2	16 ± 2	—	—	—

(a) values deduced from the plots of Figs. 5 and 6. (b) if the dilution at constant lamellae occurs, d_o is the thickness of the "dry" lamellae; otherwise see discussion in text

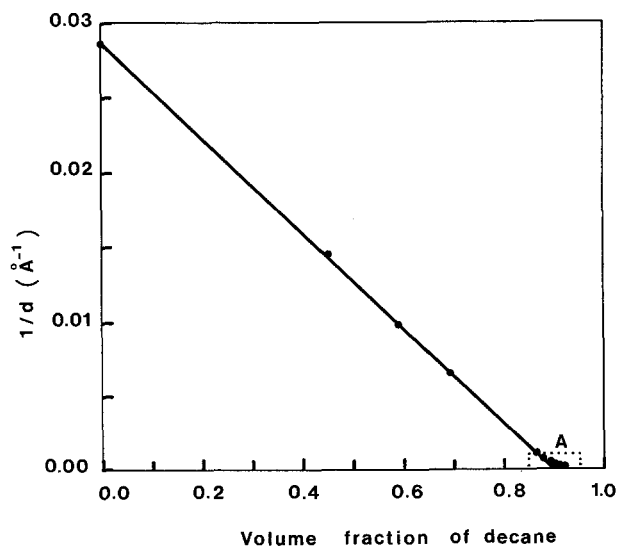


Fig. 5. Plot of $d = 2\pi/q_b$ as a function of the volume fraction of decane for samples of set I; ●: samples of sets II and III in the portion A of this graph are shown enlarged in Fig. 6. The straight line is the least squares fit to the points belonging to set I

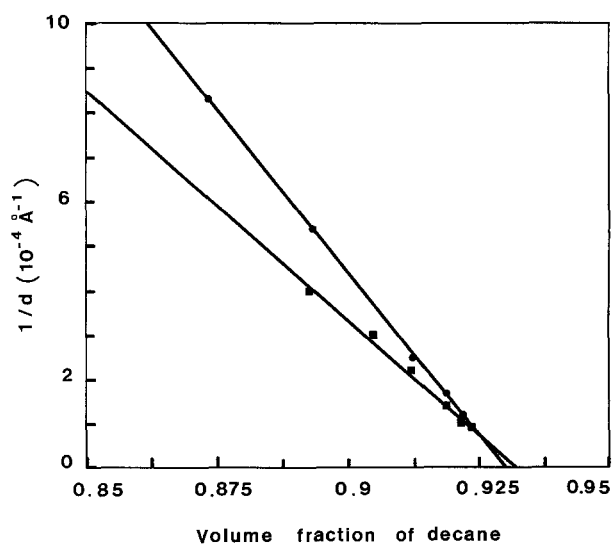


Fig. 6. Enlargement of the portion A of Fig. 5; plot of $d = 2\pi/q_b$ as a function of the volume fraction of decane for samples of set II: ●, and of set III: ■. The straight lines are the least squares fit to the points belonging, respectively, to sets II and III

pattern with dilution is analogous to that of the brine swollen LLC previously studied [4, 15]; the progressive growth of the central scattering, together with the disappearance of the Bragg singularity, can be traced back to the thermally induced displacement of the lamellae leading to concentration fluctuations as discussed in [15]. In this context the observed patterns seem to indicate that in the decane + pentanol swollen LLC the positional order is softer than in the brine swollen LLC previously studied.

In the extremely dilute regime, the situation is less clear cut. Owing to the very narrow domain of existence and to the extreme dilution of the samples it is difficult to ascertain whether the above analysis is valid and brings convincing proof that the swelling of the LLC occurs with constant lamellae. This is even more difficult to ascertain because the obtained values for the lamellae composition and the apparent thickness (cf. Table 1) are difficult to reconcile with a plausible arrangement of molecules in the lamellae. This arrangement could be either analogous to the one postulated in the dilute LLC [14] where the lamellae consist of water entrapped between two monolayers containing OBS + pentanol, but this is impossible with the obtained composition and d_o . Or it could be a different (although difficult to imagine) arrangement consistent with the molecular properties of OBS, pentanol, and water.

If we first make the hypothesis that we do indeed have a swelling at constant lamellae:

i) Either the large apparent thickness of about twice that observed in the swollen LLC and the larger pentanol content in the lamellae could be accounted for by the existence in the lamellae of defects such as holes. In that case pentanol and OBS could be distributed unevenly between the flat and curved portions of the two monolayers, entrapping water in a way analogous to that demonstrated in a lyotropic smectic phase [18]. The fact that the swelling appears to be at constant lamellae implies that the proportion of holes in the lamellae is constant. The existence of these holes should be manifest in the SAXS pattern (observed perpendicularly to the lamellae) from oriented samples free of other defects; work is currently in progress to obtain such samples.

ii) Or an alternative explanation could be that the lamellae become very crumpled. In that case it is straight forward to show that:

$$d_o = \frac{S'}{S} \delta$$

where δ is the true lamellae thickness, S' is the real surface of a lamella, and S the projection of this surface on a plane perpendicular to the axis of the stack of lamellae. Of course $S' > S$, so that the apparent thickness can be much larger than the true thickness.

Another possible explanation could be as follows: OBS is but very slightly soluble in decane, however at these extreme dilutions even a very small solubilization of OBS in decane (eventually enhanced by the presence of pentanol) would lead to a net decrease of the true volume fraction of the lamellae, an effect totally negligible in more concentrated samples. Consequently, the conclusions concerning the composition of the lamellae drawn above from the experimental data would be false and an overestimation of the lamellae thickness would arise.

A question remains, no matter the structure of the lamellae, namely what interaction can be responsible for the observed lamellar order which becomes, as already stressed, harder with dilution in extremely dilute regime? The steric interaction, which has been shown to be efficient in swollen LLC, is not expected to lead to such a behavior, at least not in the harmonic description usually given [12]. Some other explanation must be sought for:

i) A first possibility is that the small amount of OBS solubilized is not the neutral OBS but the amphiphilic ion, the sodium counterion remaining within the lamellae. This would result in a net electric charge on the lamellae and the resulting long-range repulsive interaction could be responsible for the smectic order in this extremely dilute regime in a way analogous to that discussed in [5, 19] for water-swollen LLC.

ii) Alternatively, anharmonic corrections introduced in the calculation of the steric interaction could lead to the observed hardening of the lamellar order as described by Sornette [20]. In this description the evolution from swollen to extremely swollen LLC would be an illustration of what is termed the "softening transition", the steric interaction being responsible for the stability of the LLC in all its domain of existence.

In conclusion let us state that a thorough understanding of this extremely swollen lamellar phase with so peculiar characteristics is still a challenge.

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