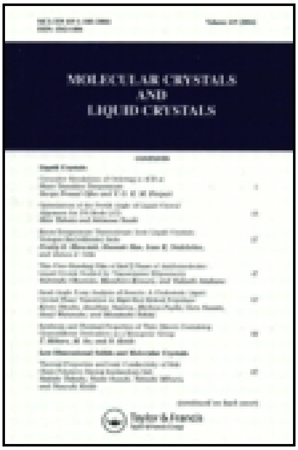

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Experimental Study of Swollen Lyotropic Lamellar Phases

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EXPERIMENTAL STUDY OF SWOLLEN LYOTROPIC LAMELLAR PHASES

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Abstract The behavior of lyotropic lamellar phases is studied upon the dilution by water (or brine) or oil. When diluted with brine, the phases exhibit a simple swelling behavior but the scattering patterns differ when the surfactant is changed. When diluted with oil, the smectic order persits and seems to become "harder" for hyper swollen phases (repeat distance ~ 6000 Å).

INTRODUCTION

Most of lyotropic systems (ternary or quaternary) give rise to a lamellar phase. In contrast with thermotropic smectics, they can be swollen, that is the periodicity can be varied by adding the good diluant which can be water (brine) or oil (1-5). In the first case, the hydrophobic layers are separated by water and addition of water only results in an increase of the periodicity without any change in the hydrophobic layer. In the second case, it is the hydrophilic layer which remains unchanged.

The stability of these swollen lamellar phases up to dilutions where the average interlamellar distances can be 40 times the individual hydrophobic layer thickness for instance, is now well theoretically studied (6,7). It is in particular shown that the asymptotic behavior of these systems is quite different according as there are electrostatic interactions or not (8).

We present here experimental investigations on lamellar phases using X-rays, Neutrons and light scattering. In systems involving brine, the first order Bragg peak has been followed up to repeat distances of about 1100 Å. In systems where the solvent is oil, the two first Bragg singularities can be observed with light scattering ; they correspond to an interlamellar distance of 6500 Å. These observations are qualitatively in agreement with theorical predictions but the specific behavior observed between systems swollen by brine is not yet understood.

WATER OR BRINE SWOLLEN LAMELLAR PHASES

As said above, the presence or absence of an unscreened long range electrostatic potential (which scales as d^{-1}), should lead to strong differences of behavior of the systems upon dilution. The studied systems are : *i*) cetylpyridinium chloride

(CPCl) /hexanol/brine (0.2 M NaCl), *ii)* Sodium octylbenzene sulfonate (OBS)/n-pentanol/brine (0.5 M NaCl) and *iii)* n-dodecylbetaïne/n-pentanol/water. In these systems, electrostatic interactions do not play any role. In the two first ones the electrostatic repulsions are strongly screened by the free ions of the solvent (Debye length ≤ 7 Å) and in the last one, the surfactant is a neutral zwitterionic molecule (the individual lamellae is neutral).

EXPERIMENTAL RESULTS

Three experimental setups were used. The first one is a classical Small Angle X ray Goniometer with a position sensitive counter. The collimation can be considered as punctual. Micrographs are obtained at the synchroton radiation Laboratory L.U.R.E at Orsay on line D16 (punctual collimation). For the most diluted samples, experiments were done at I.L.L (Grenoble) on line D 11. In all cases the samples consist of Lindemann capillaries where a cylindrical alignment (checked by microscopy) is obtained by a surface treatment (9). The focal conics observed in non oriented samples confirm the lamellar structure.

Figures 1, 2, 3 show the evolution of the X ray scattering profile for the three systems with the dilution. It can be seen

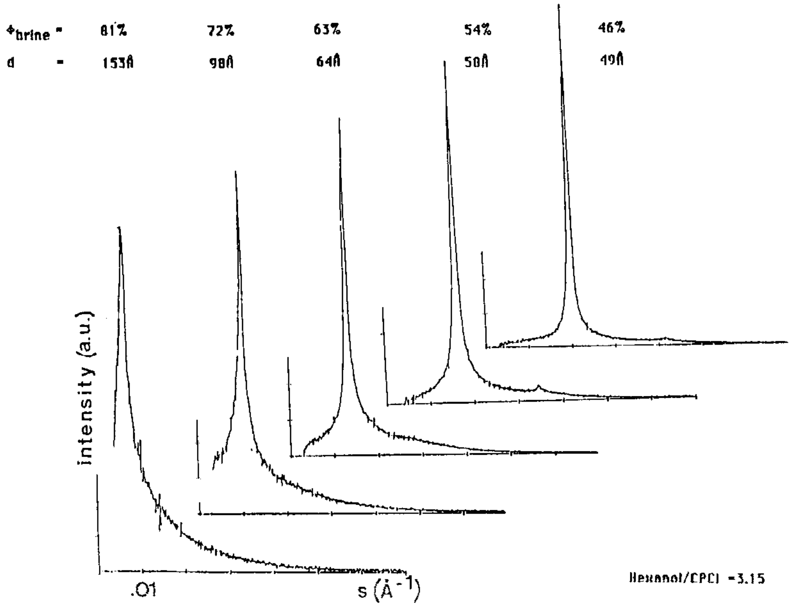

Figure 1 : evolution of the scattering profile for CPCl.

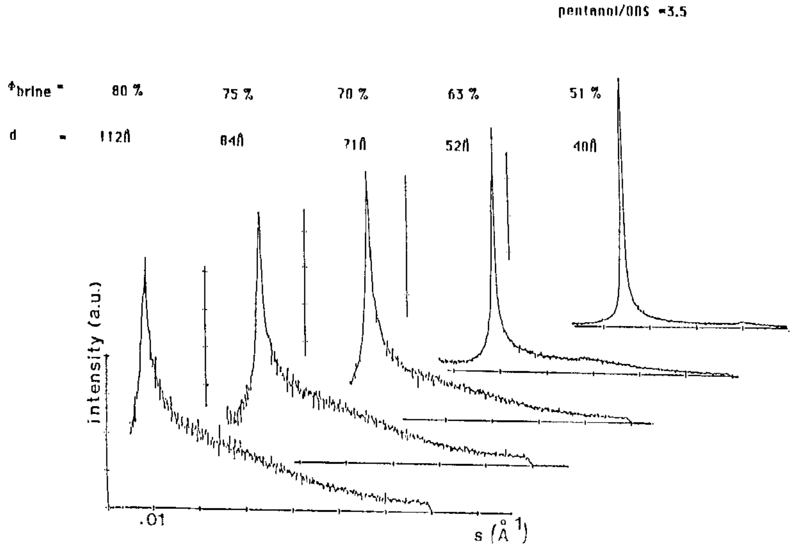

Figure 2 : evolution of the scattering profile for OBS.

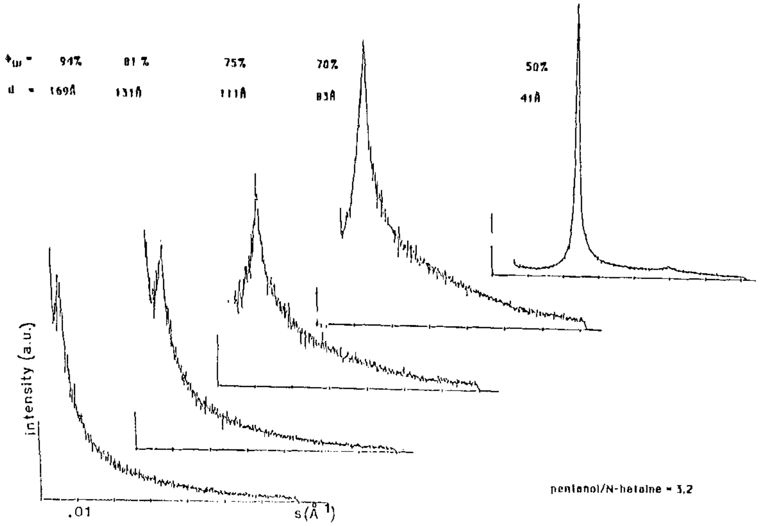

Figure 3 : evolution of the scattering profile for Betaïne.

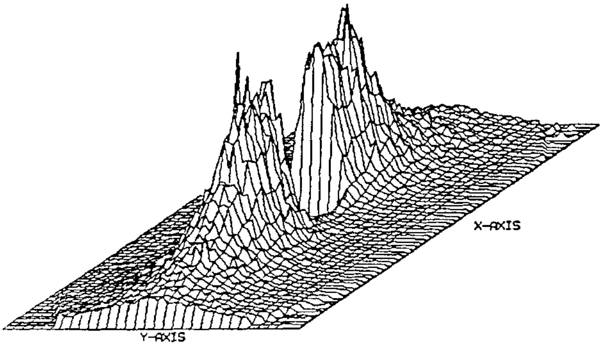

Figure 4 : 2 D Neutron spectrum. The repeat distance is 970 Å.

that the general behavior is quite similar. For the most concentrated solutions there are two Bragg peaks in the ratio1/2(in favor of lamellar structure). The second order Bragg peak disappears under dilution while the tail of the first order broadens.On the other hand, the variation of the repeat distance given by $1/d = s_m$ ($q_m = 2\pi s_m$ is the scattering vector of the first Bragg maximum) shows that the lamellar phase is an expanding one. This means that the repeat distance is given by (ϕ_w is the volume fraction of water) :

$$1/d = 1/d_a\,(1 - \phi_w)$$

where d_a is the thickness of the hydrophobic layer which remains unchanged when the lamellar phase is diluted. This is in agreement with the radial geometry of the phase diagram of these systems (2,9, 10) which involves that any line starting from the brine corner is a dilution line.

A Small Angle Neutron Scattering study was performed on the system CPCl/hexanol/brine. It shows that the quasi long range order (Bragg peak) (figure 4) and the pure swelling behavior(figure 5) persists even for repeat distances of 1100Å. Moreover, the optical birefringence at rest of the phase at these dilution rates indicates that long range orientational order also persists.

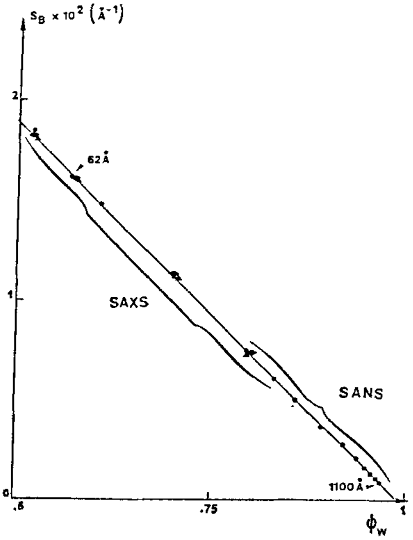

Figure 5 : position of the Bragg peak (s_m=1/d) as a function of the brine volume fraction for the system CPCl/hexanol/brine.

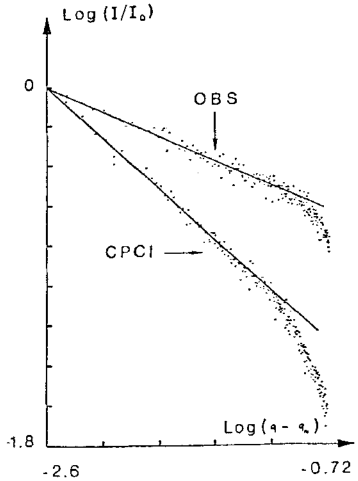

Figure 6 : Log-Log plot of the intensity as a function of q-q_m for OBS and CPCl samples with ϕ_w = .75.

Nevertheless, a more quantitative study of X ray experiments seems to indicate that there is a specificity. Indeed, the intensity near the Bragg peak exhibits a power law behavior $I \propto (q - q_m)^{-\nu}$

TABLE I The exponent ν for the power law singularity as a function of the dilution.

$\varkappa = a\,(1 - \delta/d)^2$ where δ is the thickness of the swollen membranes ($\nu = 2 - \varkappa$).

CPCl				OBS				Betaine			
ϕ_w	d(Å)	ν	a	ϕ_w	d(Å)	ν	a	ϕ_w	d(Å)	ν	a
0.49	49	> 0.9	> 2.85	0.51	40	> 0.9	> 2.57	0.50	41	> 0.9	> 3.9
0.62	64	> 0.9	1.75	0.63	52	0.61	2.46	0.70	83	0.32	2.4
0.66	73	0.75	1.85	0.70	71	0.46	2.07	0.75	97	0.21	2.3
0.75	98	0.66	1.58	0.75	84	0.33	2.06	0.78	110	-	
0.83	153	0.64	1.26	0.80	112	0.33	1.76	0.82	131	-	
								0.84	169	-	

The exponent ν varies in this concentration range with the dilution for all the systems (table I) but, for a given volume fraction of diluant, its value depends on the system (table I, figure 6). The broadening of the tail of the Bragg singularity is less pronounced if one considers successively the n-dodecylbetaïne, the OBS or the CPCl and consequently the exponent increases. The exponent seems to tend towards a limit but it can only be obtained with our X- ray setup (and not in

Neutron experiments owing to the low resolution of line D 11). v is not known for repeat distances higher than 200 Å and we thus cannot know if the limit is reached.

This specificity is also observed on the micrographs obtained at L.U.R.E (figure 7 and 8). Here we have a 2 D recording of the scattering pattern. In the plane normal to the axis of the capillaries (*i.e* containing the normal to the smectic layers) one finds the expected Bragg singularities but, in the case of the OBS samples, a large diffuse pattern appears like "butterfly wings" while in the CPCl case the scattering remains close to the Bragg peak.

DISCUSSION

The stability of a stack of lamellae is driven by several types of interactions (6 - 8) : attractives ones, namely Van der Waals interaction for which the potential scales as d^{-4} for non-retarded forces, and repulsive ones, namely the electrostatic and short range hydration forces. In order to explain the existence of infinitively swollen lamellar phases, one can introduce an effective steric interaction (3 -8) resulting from thermal fluctuations of the lamellae as introduced by Helfrich (11).

In the case of screened electrostatic interactions, the

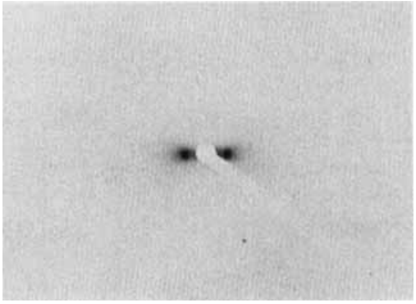

Figure 7 : 2D micrograph for CPCl sample (ϕ_W=.75)

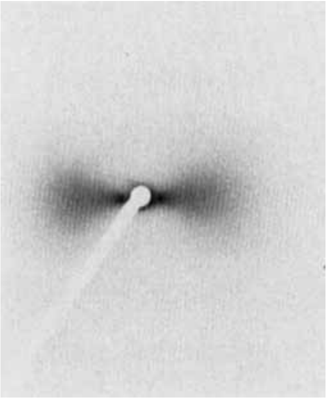

Figure 8 : 2D micrograph for OBS sample (ϕ_W=.83).

potential between two charged membranes decays exponentially ($V \propto \exp(-d/\lambda_E)$ where λ_E is the Debye length) and thus results in a very short range interaction. In that case, it is shown (8) that the interactions in the unbound regime lead to a quasi long range translational order in the lamellar structure. We have seen that all our studied systems are systems where electrostatic interactions must not occur ; the persistence of Bragg peaks up to high dilution of the three lamellar phases proves the long range character of the Helfrich's steric interaction.

Nevertheless, theory also predicts that this quasi long range order is characterized by an exponent $\varkappa$ describing the decay of correlations, this exponent being a pure number independent (asymptotically) on the repeat distance. This results (3, 12, 13), for the scattered intensity, in a singularity with a power law behavior (instead of a classical δ function)

$$S(0,0,q_z) \propto (q_z - q_m)^{-(2 - \varkappa)}$$

where the exponent $2 - \varkappa$ is asymptotically universal and thus not system-dependent (14). Table I shows off the difference between the exponents (and that even if the limit of ν is not yet reached). At such dilutions the finite thickness δ of the hydrophobic lamella must be taken into account. Then, the exponent $\varkappa$ takes the form $\varkappa = a(1 - \delta/d)^2$ where a is a pure number equal to 1.33 (5 - 11). It can be seen that the CPCl system seems to tend towards the expected behavior as the systems of Safinya et al but it is not the case for the two other systems. This discrepancy is not understood. It just appears from micrographs aspect that the out of plane fluctuations of the lamellae are larger in the case of "soft" systems (OBS) than in "hard" systems while the orientational fluctuations have, for both systems, a small amplitude (9).

OIL SWOLLEN LAMELLAR PHASE

EXPERIMENTAL RESULTS

We are here dealing with a quaternary system : OBS/n-pentanol/water/Decane. The individual lamella is now made of a water layer sandwiched between two layers of surfactant and the diluant is the oil or, more precisely, decane plus few percents pentanol (15). A lamellar phase can be obtained, for instance, starting from the lamellar phase found in the ternary system (without oil) and by adding the adequate diluant. Such a swelling procedure has been performed up to dilution such as the resulting phase contains 0,7% (volume fraction) of the initial liquid crystal. The orientational order is here also showed off by optical birefringence. At such a dilution, the repeat distance should give a Bragg diffraction pattern of light. Light scattering experiments performed on cylindrically aligned samples allow us to obtain two well defined Bragg peaks in the ratio 1/2 with a repeat distance d ≈ 6500 ± 300 Å (the spacing of the initial liquid crystal is 35 Å).

DISCUSSION

The obtention of two well defined peaks for this hyperswollen lamellar phase, while for dilution corresponding to spacing of the order of 100 Å-200 Å the diffraction profile and its evolution are very similar to those obtained in brine swollen lamellar phases is quite surprising. Moreover, for these last dilutions, a small angle X ray scattering progressively appears under dilution while such a small angle scattering does not exist at very high dilution. All these experimental evidences show that : *i*)a quasi long range positional order persists for very high dilutions and *i i*) it seems that there are two behaviors for the two ranges of swelling (d ~ 200 Å and d ~ 5000 Å), the most diluted liquid crystal being "harder" than the less diluted. Such a behavior draws near the behavior of "electrostatic" systems as described by Leibler (8). In these systems, for sufficiently large d, unscreened electrostatic interactions result in a long range repulsive potential $V \propto d^{-1}$.

This leads to a dependence of $\varkappa$ on the mean lamellar spacing and consequently $\varkappa$ vanishes : asymptotically the exponent of the power law followed by the Bragg singularity must be equal (for powder samples) to - 2. Such a behavior could be observed in systems swollen by oil (16).

CONCLUSION

The main results of this experimental study are : *i*) for non electrostatic systems, the lamellar phase is an expanding one but our systems present a specificity not yet explained *ii*) for systems swollen with oil, the positional order persists for very high dilution, this order becoming "harder" for hyper swollen phases.

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