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Effects of Shear on a Lyotropic Lamellar Phase

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We have investigated the steady-state rheological behaviour of the lamellar phase of a dilute lyotropic system (CPCl, hexanol, brine). In accordance with previous measurements in another lyotropic system[1], we obtain a power-law dependence of the viscosity as a function of the shear-rate ($\eta \sim \dot{\gamma}^{-\alpha}$). In our case, α does not depend on the brine volumic fraction ϕ in each of the ranges $\phi<0.77$ ($\alpha \sim 0.45$) and $\phi>0.78$.($\alpha \sim 0.8$) displaying a rather abrupt change between them. In situ X-ray measurements and optical microscopic observations show that the steady-state textures obtained under shear are different above and below $\phi \sim 0.78$.

Keywords: lamellar; defects; shear-thinning; rheological instabilities

INTRODUCTION

The rheological behavior of lamellar phases is a subject of intense investigations in thermotropic[2], polymeric[3] and lyotropic[1] systems either for the nature of the instabilities which appear under shear, or in order to understand the role of defects (dislocations, focal conic domains) in the setting up of irreversible viscoelastic properties[2]. The first subject has been

recently most active in lyotropics. For example Roux et co-workers[1] have shown that, in dilute L_α phases of the AOT/brine and SDS/pentanol/brine systems, multilamellar vesicules (spherulites or onions) were formed under relatively low shear rates. The mechanism of spherulite formation remains however unclear to a large extent. The present paper reports on the steady-state rheological behaviour of the lamellar phase of a lyotropic system made of cetylpyridinium chloride (surfactant), hexanol (cosurfactant) and brine as the solvent, in the range $0.6<\phi<0.9$. A remarkable feature of this lamellar phase is that, at rest, two ranges of dilution can be distinguished, at constant ratio cosurfactant/surfactant, according to the observed textures: the typical defects, in the more dilute samples, are multilamellar vesicules, while they are focal conic domains and oily streaks in the less dilute[4]. Also, the near-by sponge phase displays two different rheooptical behaviours as a function of the dilution[5]. We shall see that the rheological behavior of the lamellar phase is also strikingly dependent of the dilution.

EXPERIMENTAL SET-UP

Rheological measurements were performed using a rheometer DSR500 from Rheometrics ($0.4s^{-1}< \dot{\gamma} <1250s^{-1}$), equipped with a Couette cell (gap between cylinders: 0.75mm, outer radius: 16 mm).

X-ray scattering experiments and quasi-simultaneous optical microscopic observations were conducted at the D24 beam line of the LURE-DCI synchrotron radiation facility in Orsay using a Couette cell (gap between cylinders: 0.5 or 1mm, outer radius: 16mm, $0.1s^{-1}< \dot{\gamma} <3600s^{-1}$). The X-ray beam can be chosen parallel either to the shear gradient (radial geometry) or to the velocity (tangential geometry). The light beam crosses the center of the cell perpendicularly to the x-ray beam in the horizontal plane. Observations are carried out between crossed polars.

RHEOLOGICAL MEASUREMENTS

We first present rheological measurements obtained for a constant hexanol/CPCl ratio (h/c= 1.01) in the membrane, close to the biphasic region lamellar/sponge, and for different volumic fractions of brine ϕ. We impose a constant shear rate to the sample and wait for the steady-state to be established. The stationary value of the measured viscosity η is then reported as a function of the corresponding shear rate $\dot{\gamma}$.

Two different behaviours have been observed :

- **ϕ>0.78**

At the lowest and the highest shear rates, the viscosity displays a power-law dependence (Fig.1), but with different exponents: $\eta \sim \dot{\gamma}^{-0.4}$ at low $\dot{\gamma}$ (most clearly visible near $\phi \sim 0.78$) and $\eta \sim \dot{\gamma}^{-\alpha}$ $(0.7<\alpha<0.9)$ at high $\dot{\gamma}$. In the intermediary shear-rate region, the viscosity suffers a large jump.

The shear rate value at which the viscosity jump occurs ($\dot{\gamma}_0$) decreases when the membrane repeat distance increases (Fig.2).

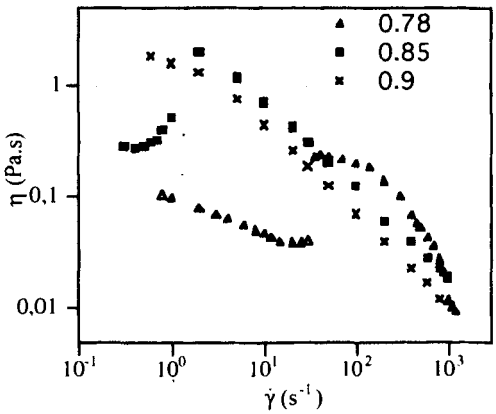


FIGURE 1 Viscosity as a function of the shear rate for different dilutions ϕ>0.78.

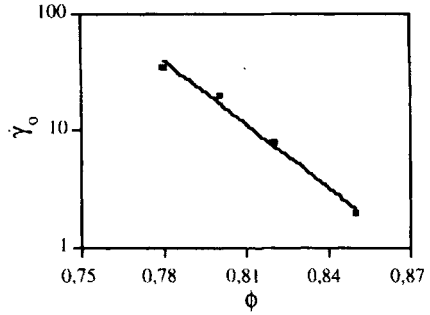


FIGURE 2 $\dot{\gamma}_0$ as a function of the dilution ϕ

- ϕ<0.77

Shear-thinning is obtained over the whole explored range of shear rates (Fig.3). Again, this dependence is characterized by a power-law ($\eta \sim \dot{\gamma}^{-\alpha}$) whose exponent α is 0.45 for the whole range of dilutions ($0.6<\phi<0.77$); no jump is observed at values of $\dot{\gamma}_0(\phi)$ extrapolated from Fig.2.

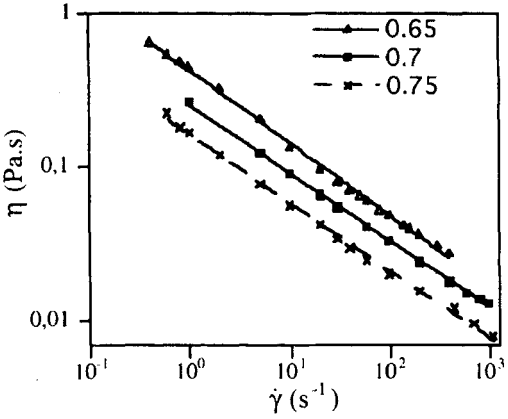


FIGURE 3 Plot of viscosity vs shear rate for different dilutions ϕ<0.77 ($0.43<\alpha<0.47$).

Nevertheless, for dilutions approaching 0.77 (ϕ<0.77), we observe strong and erratic fluctuations of the viscosity with time, occurring for shear rates close to the value $\dot{\gamma}_0$ at which we may have expected the jump.

Figure 4 illustrates such fluctuations. Increasing shear rates ($60s^{-1}$, $100s^{1}$, $140s^{-1}$, $200s^{-1}$) have been successively imposed to the same sample (ϕ=0.76) during the same time (900s). The viscosity measured as a function of time is represented. Stationary values of the viscosity are almost immediatly reached for imposed shear rates of $60s^{-1}$, $140s^{-1}$ and $200s^{-1}$ (these stationary values fit to the $\eta \sim \dot{\gamma}^{-0.45}$ curve) but fluctuations occur for $100s^{-1}$ and $140s^{-1}$ range of values $\dot{\gamma}$ at which we may have expected the jump, according to Fig.2.

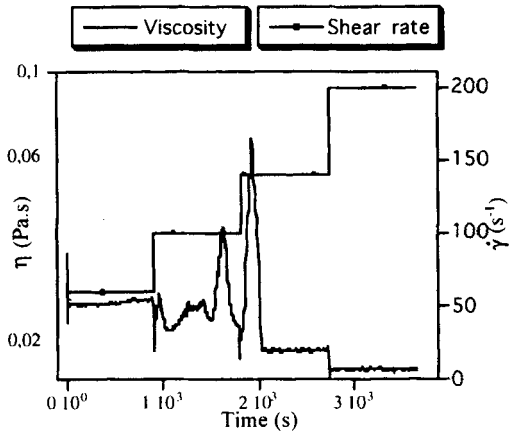


FIGURE 4 Plot of viscosity vs time for stepwise increasing shear rates ($60s^{-1}$, $100s^{-1}$, $140s^{-1}$, $200s^{-1}$) for ϕ=0.76.

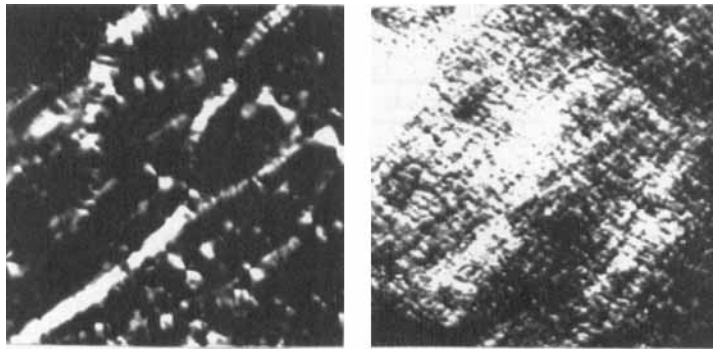
SAXS STUDIES AND OPTICAL MICROSCOPIC OBSERVATIONS

In situ X-Ray scattering experiments and optical microscopic observations (between crossed polars) have been performed to determine the structural changes of the lamellar phase under shear .

ϕ>0.78:

At low shear rates, the dominating orientation of the director (normal to the lamellae) is along $\nabla \mathbf{v}$ and the size of the initial macroscopic defects (large spherulites and focal conics possibly organized in oily streaks) decreases under increasing shear. For shear rates at which the viscosity jump was observed, 2D-spectra in radial and tangential geometries turn isotropic. The lamellar order is conserved as shown by the presence of the Bragg peak.

A granular texture appears (Fig.5). These results suggest the formation of multilamellar vesicules as already observed by Roux et al. in other systems.



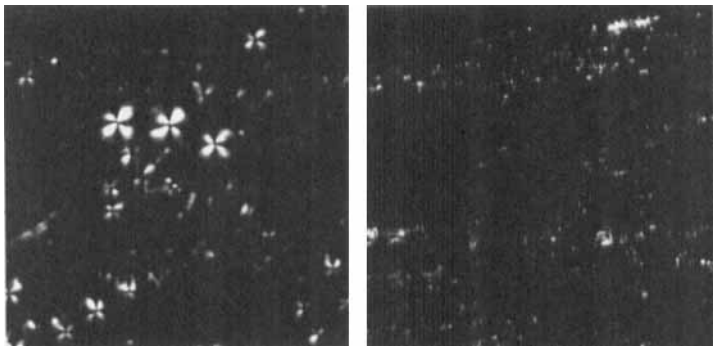
(a) (b)

FIGURE 5 Photographs before (a) and after (b) the viscosity jump, ϕ= 0.78, (a): $\dot{\gamma}$=1s^{-1}; (b): $\dot{\gamma}$=35s^{-1} (magnification: x200).

ϕ<0.77:

With increasing shear rates, the orientation of the layers parallel to the cylinders is more and more dominating over both other ones (parallel to ($\mathbf{z}$, $\nabla \mathbf{v}$) or to ($\mathbf{v}$, $\nabla \mathbf{v}$)), probably to facilitate the flow. But an isotropic spectrum is never observed.

Visual observations show initially the presence of focal conics possibly organized in oily streaks. With increasing shear rate, oily streaks tend to align along the flow direction and to thin (Fig. 6) but there is no appearance of the spherulitic texture.



(a) (b)

FIGURE 6 Photographs at different shear rates. ϕ= 0.70, (a): $\dot{\gamma}$=0.2s^{-1}; (b): $\dot{\gamma}$=80s^{-1} (magnification: x200).

DISCUSSION AND CONCLUSION

In our system, the formation of spherolites under shear is obtained only for the most diluted samples while in the case of systems studied by Roux and coworkers, it was observed independently of the dilution of the lamella.

The defectless lamellar phase obtained for the highest shear rates and characterized by a newtonian behaviour according to Roux et al., was not observed in our case, maybe because of the limitations of the rheometer ($\dot{\gamma}_{max}$=1250s^{-1}).

Another difference is the shear-thining ($\eta \sim \dot{\gamma}^{-0.4}$) that we observed for the lowest shear rates, before the viscosity jump (ϕ>0.78), while Roux and al. mentionned a newtonian behaviour. This power-law behaviour, also obtained for concentrated samples (ϕ<0.77) in the whole explored range of shear rates, seems to characterize the flow of a lamellar phase full of focal conics and oily streaks, while $\eta \sim \dot{\gamma}^{-0.8}$ is associated with the presence of a spherulitic texture.

Approaching the limit between both domains of concentration from the more concentrated samples side, the observed fluctuations of viscosity may indicate the presence of an instability which is not strong enough to transform into a spherulitic texture. We are carrying on the study of this supposed instability to characterize the parameters involved in the formation of spherulites.

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