

Closed compact Taylor's droplets in a phase-separated lamellar-sponge mixture under shear flow

L. COURBIN, G. CRISTOBAL, J. ROUCH and P. PANIZZA(*)

Centre de Physique Moléculaire Optique et Hertzienne, UMR 5792

Université Bordeaux I - 351 Cours de la Libération, Talence 33400, France

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Abstract. – We have studied by optical microscopy, small-angle light scattering, and rheology, the behavior under shear flow of a phase-separated lamellar-sponge (L_α - L_3) ternary mixture. We observe in the L_α -rich region ($\Phi_{L_\alpha} > 80\%$) the existence of a Newtonian assembly made of closed compact monodisperse lamellar droplets immersed in the sponge phase. Contrary to the classical onion glassy texture obtained upon shearing L_α phases, the droplet size scales herein as $\dot{\gamma}^{-1}$, the inverse of the shear rate. This result is in good agreement with Taylor's picture. Above a critical shear rate, $\dot{\gamma}_c$, the droplets organize to form a single colloidal crystal whose lattice size varies as $\dot{\gamma}^{-1/3}$.

To the memory of Tess Melissa P.

Introduction. – In the last few years, the effect of shear flow on complex fluids has drawn much attention not only because of their large practical use in everyday life but also because of fundamental interest [1,2]. Due to their large characteristic length scales, these fluids present unusual strong couplings between their texture and the flow, which do not exist in simple fluids. Predicting the rheological properties of such materials represents therefore a real theoretical challenge in the field of non-equilibrium physics. One of the most striking examples of such effect is certainly the formation of a glassy assembly made of multilamellar vesicles, known in the literature as the “onion texture” [3], obtained upon shearing a lamellar phase. These vesicles are monodisperse and their volume fraction is 100%. Their size, which varies as $\dot{\gamma}^{-1/2}$, where $\dot{\gamma}$ is the shear rate, can be tuned continuously from a few microns to a few tenths of it [4]. Under certain conditions, this assembly may even exhibit a long-range order [5], similar to the layering observed in colloids [6].

Large efforts have been devoted to describe the effect of shear flow on L_α phases [7,8] and to characterize the properties of “onion textures” [9,10]. The formulation of multilamellar vesicles according to this experimental procedure has now led to various applications in drug delivery, biochemistry catalysis and cosmetics. Yet, the physical mechanisms leading to the onion formation [11,12] and governing the droplet size [4,13,14] remain still unclear and under significant debate. Very intriguing is also the non-Newtonian behavior of the onion texture [15], which despite of being well characterized is not yet understood [16].

(*) E-mail: ppanizza@cribx1.u-bordeaux.fr

In this paper, we report the formation of monodisperse multilamellar droplets upon shearing a phase-separated ternary mixture consisting of lamellar (L_α) and sponge (L_3) phases. In the L_α -rich region, the shear-induced texture resembles the classical onion texture since the observed lamellar droplets are monodisperse and beyond close-packing. However, contrary to classical glassy onion textures found by Roux *et al.* [3,4], the texture presented herein exhibits a quasi-Newtonian behavior and the size of the vesicles varies as the inverse of the shear rate. We propose a simple model based on Taylor's pioneering work on dilute emulsion [17], to explain the quasi-Newtonian behavior of the mixture and the variation of the droplet size with shear rate.

Experimental system. – We study solutions containing 20% by weight of AOT (sodium bis(2-ethylhexyl) sulfosuccinate, obtained from Fluka) and 80% by weight of brine with different sodium chloride content. Gosh and Miller have already published in detail the whole equilibrium phase diagram of this system [18]. Figure 1 shows the succession of the phases encountered as a function of salinity when the surfactant weight fraction is 20% and the temperature is 25 °C. At low salt ($c < 1.5$ wt%) content, the system is a lamellar phase (L_α), which consists of bilayers of surfactant separated by water. At high salt content ($1.9\% < c < 2\%$), a sponge phase (L_3) is observed. For intermediate salt concentrations ($1.5 < c < 1.9\%$), coexistence between L_α and L_3 phases is observed. In this region of the phase diagram, the volume fraction of the L_α phase can be tuned continuously from 100% to 0% by simply increasing the salt content. This system is very sensitive to the purity of the chemical used. As a result, slight translation of the transition salinities can be observed. Both L_α and L_3 phases are constructed by the same bilayers and are distinct only by the packing of the bilayers into space. Whereas the bilayers in the L_α phase are stacked with a smectic order, the L_3 phase is made of a disordered multiply connected bilayer that divides the solvent volume into two equivalent subvolumes [19]. Yet, the rheological behavior of both phases differs drastically: L_3 phases are usually Newtonian low viscous fluids while L_α phases exhibit strong non-Newtonian behavior [17] and viscoelastic properties [20] as a result of the formation of the onion texture under shear flow [4].

Lamellar phase region. – First, we have revisited the effect of shear flow on the lamellar phase region of this system ($c < 1.5\%$). In agreement with Roux *et al.* [3,4], we have checked that the formation of glassy onion texture (characterized by a ring, slightly elongated along \bar{Z}) in small-angle light scattering, see insert in fig. 2) occurs whatever the control parameter is stress or shear rate. When the shear rate is imposed, the transient time to reach the stationary state is very long (typically more than a dozen hours). Figure 2 shows the variation of the steady onion size with the applied shear rate, $\dot{\gamma}$, and the salinity. The size scales as $\dot{\gamma}^{-1/2}$ and increases very rapidly with the salinity. In the absence of a model to explain the formation of the onion texture, this latter behavior is hard to interpret. However, its feature is not totally surprising within the frame of Roux's model [4] which predicts that the onion size, R , varies as $R = \sqrt{(2\kappa + \tilde{\kappa})/(\eta d \dot{\gamma})}$, where κ , $\tilde{\kappa}$, d and η stand, respectively, for mean and Gaussian elastic moduli, distance between adjacent layers and viscosity. The energy cost to form a spherical vesicle from a flat bilayer, $E_{\text{sphere}} = 2\kappa + \tilde{\kappa}$, increases when the L_3 phase is approached (*i.e.* here when the salinity increases) [19] and therefore so does R .

Lamellar and sponge phases coexistence region. – We prepared solutions in the two-phase (L_α/L_3) region and let them reach equilibrium for a few weeks. Indeed, the kinetics of macroscopic phase separation is very slow after the solution has been first prepared. In order to study the effect of shear flow on such phase-separated mixture, we followed a procedure used by Mason and Bibette to prepare monodisperse emulsions [21]. First, the L_α/L_3 mixture

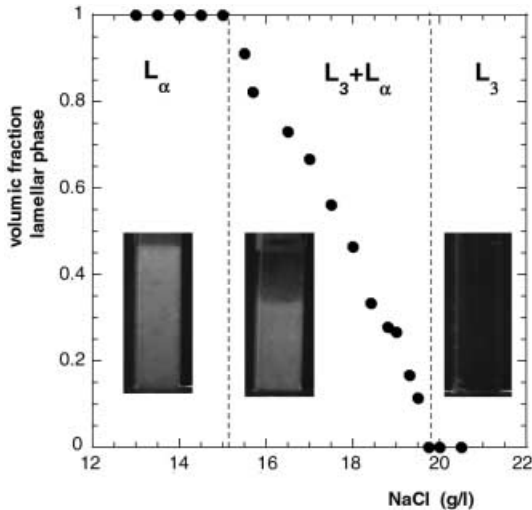


Fig. 1

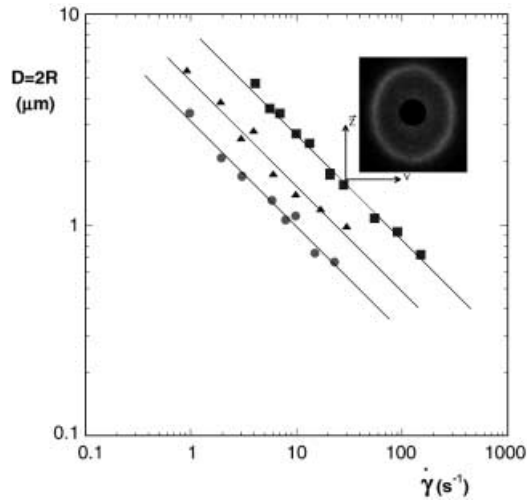


Fig. 2

Fig. 1 – Phase diagram of the pseudo binary system AOT and brine. The weight fraction of AOT is 20% and the salinity is varied. Inset: pictures of the test tubes containing the different solutions. The test tubes are placed between crossed polarizers.

Fig. 2 – Variation of the characteristic size, $D = 2\pi/q_B$ (deduced from the position of the Bragg pattern, q_B , observed in small-angle light scattering) as a function of applied shear rate. Since the onions volume fraction is 100%, D corresponds to the onion diameter. All solutions contains 20% by weight of AOT, the salinity varies. Circles, triangles and squares correspond to lamellar phases prepared, respectively, with salt content equal to 13, 14 and 15 g/l.

is gently stirred until a macroscopic homogeneous mixture is obtained. This mixture is then poured into a transparent Couette cell and sheared at constant shear rate (fig. 3). Our homemade Couette cell consists of two concentric transparent cylinders whose respective diameters are 50 and 52 mm. The outer cylinder rotates at constant angular velocity, ω , while the inner one remains fixed. The shear rate can be monitored continuously from 1 to 800 s^{-1} by merely changing the angular velocity of the rotor. A circular polarized He-Ne laser beam (wavelength $\lambda = 632.8 \text{ nm}$), parallel to the shear-gradient direction, passes through the cell and probes the sample in only one of the gaps. We observe the unpolarized scattered light on a screen located at some distance, D , of the cell (from 5 cm to 35 cm). This scattering pattern corresponding to light scattered in the velocity-vorticity plane (\bar{V}, \bar{Z}), is recorded by a video camera and digitalized for analysis. After a transient regime (varying from a few ten minutes up to a few hours depending on experimental conditions), a steady state is reached where a ring, slightly elongated along \bar{Z} , can be observed on the screen (see insert in fig. 4). Provided that the solution is macroscopically homogeneous after stirring, this steady state does not depend on initial conditions and is determined only by the value of the applied steady shear rate and salinity. The average radius of the ring indicates the existence of a characteristic size of the order of a few micrometers in the texture of the mixture. After reaching a steady state, this ring persists with the same size if one stops the shear. It may even last up to a few hours depending on experimental conditions (initial applied shear rate and salinity). The mixture appears turbid and viscous and it has the consistency of a homogeneous cream. It can then be removed from the Couette cell and placed between two glass slides for optical

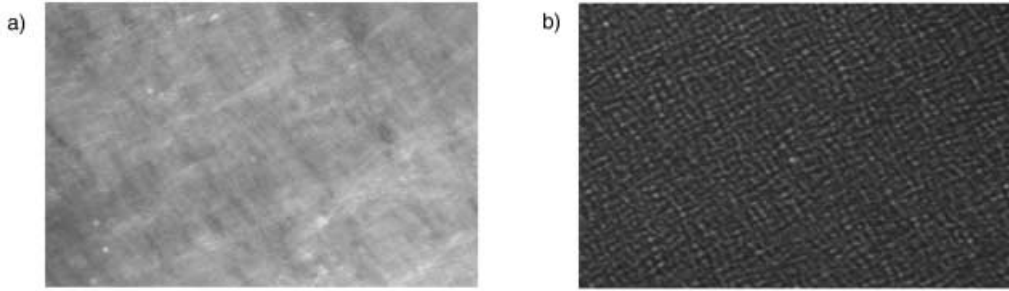


Fig. 3 – Microscope images between crossed polarizers: (a) of the premixed L_α/L_3 mixture (the salinity is 16 g/l and the AOT weight fraction is 20%); (b) of the structure of the cream transferred from the Couette cell after the premixed mixture had been sheared at 30 s^{-1} for 10 hours.

microscopy observations. After the sample has been placed between the glass slides and put into a laser beam, the same scattering ring can be observed, indicating that the shear-induced texture has not been altered by the treatment. Optical microscopy shows the existence of monodisperse multilamellar vesicles (fig. 3b), seeming rather identical to those observed by Diat and Roux in L_α phases [3,4]. The position of the Bragg scattering ring is related to the mean distance, ξ , between the centers of L_α droplets. The isotropy of the diffraction pattern shows the absence of a long-range order in the position of the monodisperse vesicles. The small deformation of the ring (typically 10%) indicates that the vesicles are slightly elongated in the direction of the flow. We have measured by light scattering the evolution of ξ as a function of $\dot{\gamma}$ (fig. 4) and have observed that $\xi \propto 1/\dot{\gamma}$. Above a critical shear rate, $\dot{\gamma}_c$, a modulation in the radial intensity of the ring emerges and leads to six well-defined Bragg peaks (see insert in fig. 4). This signature corresponds to the so-called layering transition, observed first in colloids [6] and, more recently, in some onion textures [5]. This transition, which corresponds to a crystallization of the L_α droplets in planes exhibiting a six-fold symmetry, does not affect the size since the Bragg peaks appear on the ring. Above the transition, ξ varies more slowly with $\dot{\gamma}$. It still decreases when the shear rate increases, but shows a different scaling: $\xi \propto \dot{\gamma}^{-1/3}$.

We have characterized this transition by viscosity measurements performed on a stress-controlled rheometer (SR5 from Rheometrics Scientific) using a Couette-Mooney geometry and imposing the stress. The radii of rotor and stator are, respectively, 19 mm and 19.7 mm and the immersed height is 30 mm. Figure 5 shows the variation of viscosity as a function of steady shear rate for L_α/L_3 mixtures. Two distinct regimes are observed. Below the layering transition (*i.e.* for $\dot{\gamma} < \dot{\gamma}_c$), the L_α/L_3 phase-separating mixture presents a quasi-Newtonian behavior with a viscosity, η , about two decades higher than that of the L_3 phase alone. This behavior is quite surprising, since the droplet volume fraction is higher than Φ_c , the close-packing volume fraction for spheres (assuming that the entire lamellar phase is converted into droplets). However, the existence of a yield stress cannot be ruled out, since we have not investigated the rheological behavior at very low shear rates. (The transient time to reach equilibrium is extremely long at very low shear rates.) Above the layering transition, the viscosity, η , decreases when the shear rate increases and scales as $\dot{\gamma}^{-0.85}$.

Discussion and conclusion. – The structure of our system resembles the non-Newtonian onion texture obtained by Roux and Diat upon shearing single L_α phases [3,4]. The presence of the L_3 phase at very low volume fractions does not avoid the formation of onions but, on

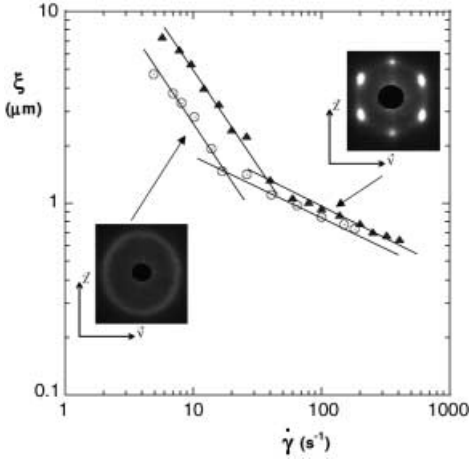


Fig. 4

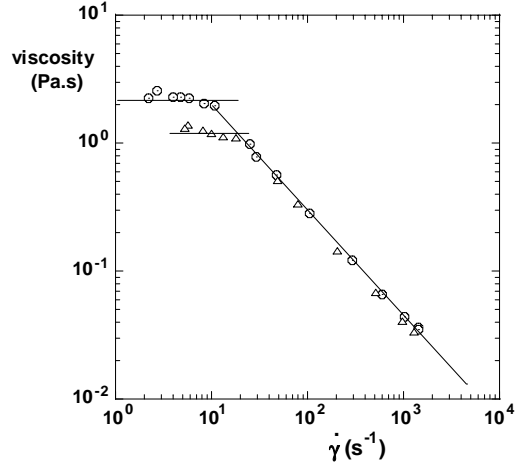


Fig. 5

Fig. 4 – Variation of the characteristic size, $\xi = 2\pi/q_B$ (deduced from the position of the Bragg pattern, q_B , observed in small-angle light scattering) as a function of applied shear rate. Both solutions contain 20% by weight of AOT, the salinity varies. Circles and triangles correspond to solutions containing 20% weight fraction of AOT and prepared, respectively, with 15.5 and 16 g/l salt content. At low shear rates, the best fits give: $\xi (\mu\text{m}) = 23.1/\dot{\gamma} (\text{s}^{-1})$ and $\xi (\mu\text{m}) = 46.9/\dot{\gamma} (\text{s}^{-1})$ for, respectively, 15.5 g/l and 16 g/l salt content. Inserts: small-angle light scattering pattern observed on a screen after shearing a premixed L_α/L_3 mixture at (a) 8 s^{-1} for 25 hours ($D = 25 \text{ cm}$) and (b) 30 s^{-1} for 10 hours ($D = 5 \text{ cm}$).

Fig. 5 – Viscosity vs. shear rate for (L_α/L_3) mixtures containing 20% of AOT in weight % and with salinity equal to 15.5 g/l (circles) and 16 g/l (triangles). At low shear rates, both solutions are Newtonian and their viscosity is, respectively, 2.19 Pa s and 1.14 Pa s.

the other hand, it drastically alters the scaling with shear rate of ξ and η , as a result of surface tension. This effect is particularly important at low shear rates where viscosity measurements, optical microscopy and small-angle scattering suggest that the L_α phase droplets are immersed in the L_3 phase. Within this picture and assuming that the entire lamellar phase is converted into droplets, the volume fraction of the L_α phase, Φ_{L_α} , is given by $\Phi_{L_\alpha} \approx (2R/\xi)^3$. Therefore the variation with shear rate of the average droplet size, R , is identical to that of the lattice size ξ (*i.e.* $R \propto 1/\dot{\gamma}$). Besides, since the lamellar phase volume fraction is nearly unity, $R \approx \xi/2$. When R is higher than a critical size, $R^* = \frac{(\tilde{\kappa} + 2\kappa)}{d \cdot \sigma}$ (where σ is the surface tension), the elastic energy of the droplet ($\propto R$) is overcome by its surface energy ($\propto R^2$). It results that the droplet size R is governed by a balance between surface tension and viscous stress according to

$$R \approx \sigma / (\eta_M \dot{\gamma}) \quad (1)$$

(where η_M is the viscosity of the mixture). When the mixture is Newtonian, and very surprisingly this seems to be the case of our system although the droplets are well beyond close packing (and therefore polyhedral), this relation yields $R \propto 1/\dot{\gamma}$. This is what we observe at low shear rates. The previous relation (1) was obtained about 70 years ago by Taylor [17] for very dilute droplets and it is worth noticing that it still holds here for a very dense system. A similar relation (1) has been used by Mason and Bibette [20] and by Bergenholtz and Wagner [14] to explain the variation of droplet size, R , with $\dot{\gamma}$ in, respectively, high volume fraction

emulsions and classical onion texture. However, the concentrated emulsions [20] and the classical onion textures [14] are highly non-Newtonian and therefore in these systems R does not scale as $1/\dot{\gamma}$. Inserting the experimental values of the viscosity, the size and $\dot{\gamma}$ in relation (1) leads in our case to an estimation of the surface tension between L_α and L_3 phases of the order of $3 \cdot 10^{-5} \text{ J m}^{-2}$. This value is in good agreement both with experimental estimations made in other systems [21, 22] and with numerical estimation from a rough dimensional analysis: $\sigma \approx k_b T/d^2 \approx 10^{-5} \text{ J m}^{-2}$ (where d and $k_b T$ are, respectively, the smectic distance (of the order of 100 \AA), and the thermal energy). Let us now try to understand why our system appears quasi-Newtonian. If we assume that the L_3 phase lies outside the lamellar droplets and the deformation is localized between droplets, a crude model, neglecting Plateau's borders, leads to a local effective shear rate of $\dot{\gamma}_{\text{eff}} \approx \dot{\gamma} f(\frac{\xi}{2R}) \approx \dot{\gamma} \frac{1}{1-\Phi_{L_\alpha}^{1/3}}$. This corresponds to an overall viscosity

$$\eta \approx \eta_{L_3} / (1 - \Phi_{L_\alpha}^{1/3}), \quad (2)$$

independent of applied shear rate (Newtonian behavior), decreasing with Φ_{L_α} and, for Φ_{L_α} close to unity, much higher than the solvent viscosity. From the two curves depicted in fig. 5 we can check the scaling of the viscosity with the volume fraction, since the viscosity of the sponge phase is almost constant. The volume fractions we studied are, respectively, 90% and 82%. The viscosity ratio we infer from our model (eq. (2)) is 2 whereas experimentally we obtain 1.9. It has to be noticed, however, that our model leads to a viscosity of 70 mPa s for the sponge phase whereas the experimental determination for bulk is typically of the order of a few mPa s. This discrepancy is not so surprising considering the simplicity of the model and that the L_3 phase is besides confined between droplets. Taking into account this very crude model, the presence of Plateau's borders between droplets should increase the value of $\dot{\gamma}_{\text{eff}}$ since the film thickness between adjacent droplets would be narrower and therefore lead to a smaller value of η_{L_3} .

As a conclusion, we have shown that shearing an L_3/L_α phase-separated mixture results in the formation of monodisperse multilamellar vesicles. At low shear rates, the droplet size is governed by surface tension (Taylor effect) and not any longer by elasticity as for glassy non-Newtonian onion textures found in lamellar phases. It results that the droplet radius, R , scales as $\dot{\gamma}^{-1}$ and not as $\dot{\gamma}^{-1/2}$, and that the mixture seems Newtonian. At high shear rates, $\dot{\gamma} > \dot{\gamma}_c$, the droplets organize to form a six-fold colloidal crystal.

In this regime the variation of ξ with $\dot{\gamma}$ is identical to what is observed in L_α phases when crystalline onion texture exists [5]: $\xi \propto \dot{\gamma}^{-1/3}$. This scaling is a general feature of ordered multilamellar vesicles (with or without L_3 phase). As far as we know, no firm theoretical explanation has been given yet for the layering transition and for the value of the exponent. However, it is worth noticing that the crystallization occurs in our system when the onion diameter is typically $1.5 \mu\text{m}$. This corresponds within our model to a film thickness, l , between adjacent droplets: $l \approx \frac{2R(1-\Phi_{L_\alpha}^{1/3})}{\Phi_{L_\alpha}^{1/3}}$ of the order of 900 angstroms, which is a few times the value of ζ , the characteristic distance of the L_3 phase.

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