PHYSICAL REVIEW E VOLUME 62, NUMBER 3 SEPTEMBER 2000

Shear-induced structural transitions in Newtonian non-Newtonian two-phase flow

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(Received 30 December 1999; revised manuscript received 24 May 2000)

We show the existence under shear flow of steady states in a two-phase region of a brine-surfactant system in which lyotropic dilute lamellar (non-Newtonian) and sponge (Newtonian) phases are coexisting. At high shear rates and low sponge phase-volume fractions, we report on the existence of a dynamic transition corresponding to the formation of a colloidal crystal of multilamellar vesicles (or ‘‘onions’’) immersed in the sponge matrix. As the sponge phase-volume fraction increases, this transition exhibits a hysteresis loop leading to a structural bistability of the two-phase flow. Contrary to single phase lamellar systems where it is always 100%, the onion volume fraction can be monitored continuously from 0 to 100 %.

PACS number(s): 82.20.Db, 61.25.Hq, 64.70.Md

Over the last decade, the effect of shear flow on the kinetics of phase separation has received a lot of attention. After a quench in the two-phase region of the phase diagram, the mixture exhibits domains with complex morphology controlled by the viscosity difference of the two phases, the relative volume fraction, and external fields [1,2]. The competition between thermodynamics which favors the coarsening of domains and shear flow which tends to deform and rupture these domains, is a challenging problem in the physics of nonequilibrium phenomena and presents some obvious industrial interests [3–5]. Indeed the use of stirring to emulsify immiscible fluids is necessary in the processing of soft materials. The influence of shear has been extensively studied both theoretically and experimentally for critical and off-critical binary mixtures [6–9]. Far from the critical composition Min and Goldburg [4,6] have observed monodisperse droplets when the break-up size is larger than the critical droplet size. On the other hand, when the two phases are both percolated close to the critical composition, strikingly elongated domain structure phase stabilized by the shear flow (string phase) have been observed by Hashimoto *et al.* [5,8] in mildly entangled polymer solution at high shear rates. These pioneering studies have been limited to rather simple molecular or polymeric fluids in which no molecular self assembly exits as in complex fluids. Contrary to such ‘‘simple’’ fluids, complex fluids exhibit some extraordinary strong couplings between microstructure and flow due to the existence of large characteristic length and therefore time scales. Different types of structural changes induced by shear have been reported in self-assembled surfactant systems [10–14]. The formation of new structures not existing at equilibrium have even been observed [15].

Questions can therefore be addressed. What can be the behavior under shear of a two-phase system in which one of the coexisting phases at equilibrium is known to show a strong structural change under shear (for instance, formation of onions in the lamellar phase [15])? How can the shear-induced structural change in this phase affect the morphology and organization of the domains in the two-phase region of the system? Is it possible to extend the concept of shear diagram and out of equilibrium transitions [10,11,15,16,17] to describe the effect of flow on such two-phase mixtures?

To answer these questions, we have studied the two-phase region of a quaternary mixture made of water, sodium dodecyl sulfate (SDS), octanol, and sodium chloride. This two-phase region consists of a lyotropic lamellar (L_α) phase and an isotropic sponge (L_3) phase. Both phases are constructed by the same bilayers and can be distinguished only by way of the packing of the bilayers into space. The lamellar phase presents a periodical stacking of bilayers in one dimension while the sponge phase has an internal structure of randomly interconnected membranes. The rheological behavior of each phase differs, however, considerably. L_α phases are usually Newtonian at low and high shear rates, and exhibit for intermediate shear rates, a shear thinning behavior related to the formation of monodisperse multilamellar vesicules (the so-called onion phase) [15]. This texture organization of the L_α phase lead to strong viscoelastic properties [18]. On the other hand L_3 phases are usually Newtonian low viscous fluids [19].

The phase diagram of the quaternary system has already been published elsewhere [20]. A sample whose weight composition is 85.6% of water (low conductivity from Millipore) containing 20 g/l of NaCl (from Prolabo), 7.9% of octanol (from Aldrich), and 6.5% of SDS (from Prolabo), has been studied as a function of shear rate and temperature. Below 30 °C, the solution is a monophasic lamellar phase and leads to the formation of shear-induced onions exhibiting a long-range order [17], similar to the shear ordering observed in colloids. Above 39 °C, the solution is a sponge phase. In the 30 to 39 °C temperature range, L_α and L_3 phases are coexisting. Figure 1 shows the volume fraction of the L_α phase in the mixture as a function of temperature.

To observe the effect of shear on the $L_\alpha - L_3$ two-phase mixture, we have used a homemade transparent Couette cell. The rotor radius is $R_r = 26$ mm and the gap is $e = 1$ mm. The temperature of the cell is stabilized to within ±0.05 °C by using a precision water bath. A motor fixes the shear rate $\dot{\gamma}$, in the range 0 to 500 s^{-1}. A laser beam passes through the cell and the small angle scattering pattern at infinity is re-

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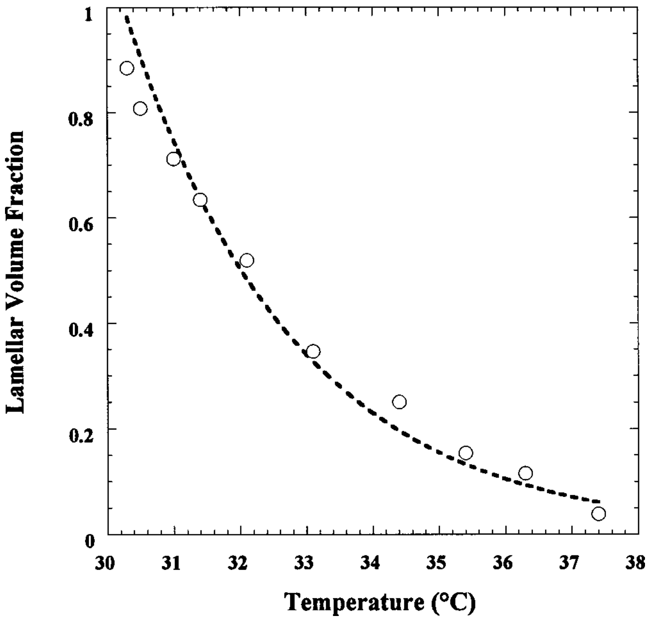


FIG. 1. Variation of the lamellar volume fraction in the biphasic mixture as a function of temperature.

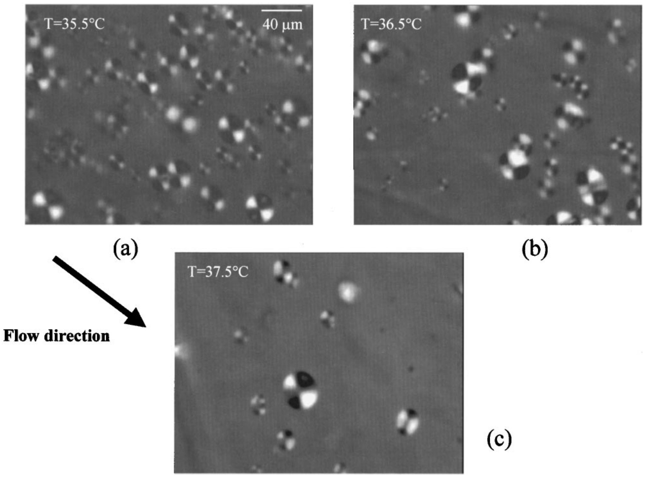


FIG. 2. Stationary texture observed under a microscope with crossed polarizers at high temperature at 150 s^{-1}. In (a)–(c) the temperature is respectively 35.5, 36.5, and 37.5 °C. By increasing the temperature, one dilutes the lamellar droplets.

corded by a video camera and digitalized for analysis. To measure the conductivity under shear flow in the velocity direction, two electrodes diametrically opposed have been mounted on the stator [21]. The conductivity is measured by a 4191A Hewlett Packard impedancemeter. No frequency dependence has been observed in the range 100 Hz to 10 MHz with or without flow. Direct microscopic observations between crossed polarizers have been performed with a cone/plate geometry on a rheovisionometer RVM 5 from Rheocontrol [22].

The system is poured into the cell and left to reach equilibrium for a few tens of mn at an initial temperature for which the solution is monophasic, i.e., $T<30\,°\mathrm{C}$ or $T>39\,°\mathrm{C}$. A rapid temperature quench is then performed under a steady shear flow in order to bring the solution to a final temperature corresponding to its two-phases ($L_\alpha - L_3$) coexisting region (30–39 °C). For low shear rates (typically below 1 s^{-1}), the solution phase separates macroscopically, whereas for higher shear rates, no apparent demixtion occurs. Instead, the $L_\alpha - L_3$ mixture tends to a homogeneous steady state, similar to an emulsion. This steady state depending on the final temperature and shear rate is independent both of the temperature and the shear histories of the system provided it has not demixted during the quench process (i.e., provided the shear rate has been always greater than a critical value). We have studied by means of conductivity, small angle light scattering, and microscopic observations, the structure of these steady states as a function of shear rate and temperature. This study allows us to distinguish three temperature regions for which the rheological behavior of the mixture differs.

High-temperature region ($T>35\,°C$). In this region corresponding to high sponge phase volume content, direct observations under shear flow reveal the existence of dilute quasi monodisperse droplets of L_α phase (Fig. 2). The radius of the lamellar droplets decreases with $\dot{\gamma}$ from typically 50 μm to 5 μm. Initially the system is driven in its two-phase state where droplets are formed. The shear ruptures then droplets which have grown to a sufficient size R which can be estimated by balancing surface droplet free energy and dissipation [6,8]. This yields to $R\approx\sigma/\eta\dot{\gamma}$ where σ and $\eta\approx10^{-2}$ Pa s are respectively the surface tension and the viscosity of the continuous medium (i.e. the L_3 phase). The experimental determination of $R=10\ \mu\mathrm{m}$ at $\dot{\gamma}=150\ \mathrm{s}^{-1}$ lead to a value of $\sigma\approx10^{-5}\ \mathrm{J\,m}^{-2}$ consistent with estimation of the literature [12].

Low-temperature region ($T<32.5\,°C$). Figure 3 shows the evolution of the conductivity as a function of applied shear rate, in the stationary regime. A sudden transition oc-

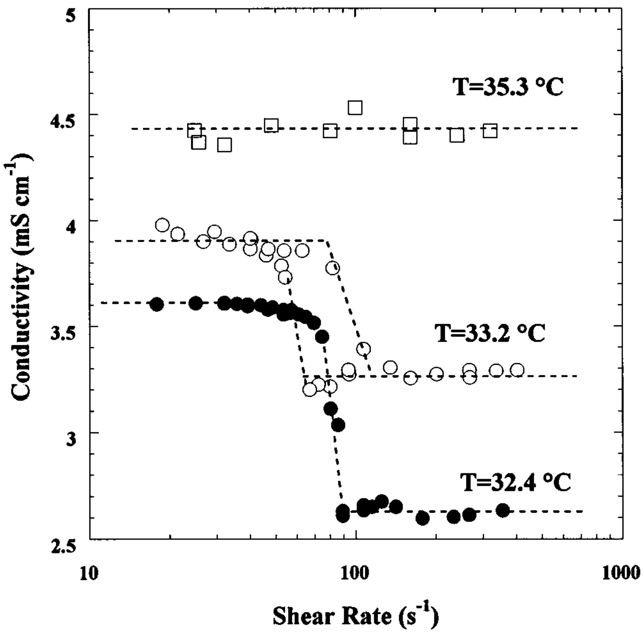
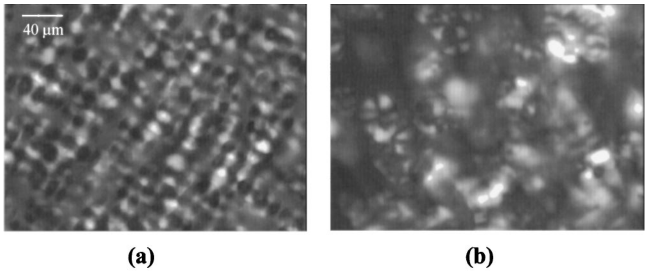


FIG. 3. Evolution with shear rate of the zero frequency conductivity measured after the quench in the lamellar/sponge coexisting mixture at different final temperatures. For each shear rate, the conductivity measurement is performed once the steady state is achieved. Closed, open circles and squares correspond, respectively, to 32.4, 33.2, and 35.3 °C.



(a) (b)

FIG. 4. Stationary textures observed under microscope with crossed polarizers at low temperature ($T=32.5\,°\mathrm{C}$) for high shear rate ($\gamma=200\,\mathrm{s}^{-1}$) (a) and low shear rate ($\gamma=30\,\mathrm{s}^{-1}$) (b).

curs at a well defined shear rate $\dot{\gamma}_c$. This transition corresponds to structural changes in the domain morphology of the mixture. When $\dot{\gamma} \geqslant \dot{\gamma}_c$, microscopic observations reveal that the texture consists of a close quasicompact assembly of monodisperse multilamellar vesicles immersed in the L_3 phase [Fig. 4(a)]. The size of the vesicles, 15 μm, does not depend on $\dot{\gamma}$. For temperatures lower than 31 °C, small angle light scattering shows the existence of sixfold Bragg peaks characteristic of a long-range ordered monocrystal (Fig. 5). However, as the volume fraction of L_3 phase increases, the solution becomes more turbid and it is difficult to observe any Bragg structure because of strong enhancement of multiple light scattering. However a FFT analysis of the microscopic texture shows a ring indicating the polycrystalline structure of the sample. When $\dot{\gamma} \geqslant \dot{\gamma}_c$, the small angle light scattering pattern presents a stretched streak in the vortex direction (Fig. 5). From a numerical analysis of the streak we can infer an elongation ratio close to 3. Microscopic images of this region show the existence of large birefringent domains elongated in the velocity direction and flowing in the L_3 phase. These domains present a few very large multilamellar vesicles (35 μm) [Fig. 4(b)].

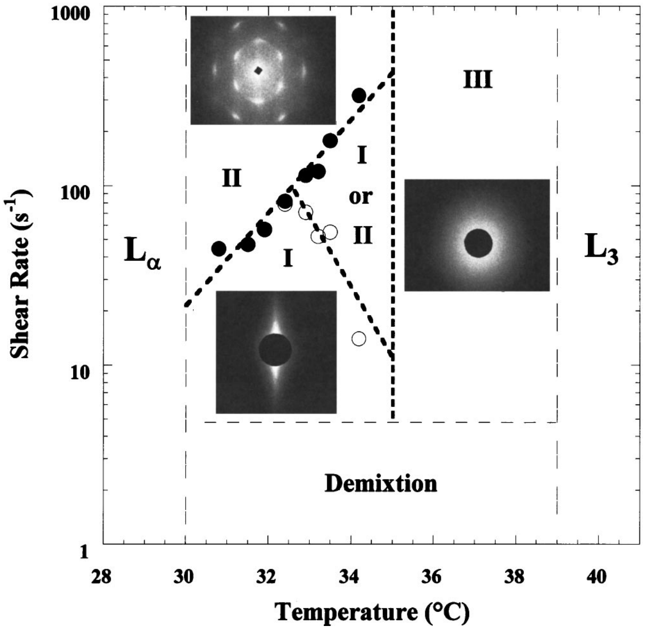


FIG. 5. Shear diagram of the mixture in the temperature and shear rate plane. Regions I, II, and III correspond respectively to the three types of stationary structure observed in the mixture: long range ordered assembly of multilamellar vesicules (low temperature, high shear rate), large multilamellar vesicules elongated along the flow direction (low temperature, low shear rate), and dilute spherulites (high temperatures). Note the existence of a bistability region between structure I and II for intermediate temperatures. The images inserted in each region represent the corresponding small angle light scattering pattern observed in the plane ($\vec{q}_v, \vec{q}_z$).

Intermediate-temperature region ($32.5<T<35\,°\mathrm{C}$). The previous shear-induced transition still exists, but now light scattering and conductivity measurements reveal the existence of a hysteresis loop (Fig. 3). The structure of the mixture at low and high shear rates is identical to the one observed in the low-temperature region. However, for intermediate shear rates, the mixture is structurally bistable. The width of this bistability region increases with temperature until 35 °C, above which no such transition is observed.

The effect of shear flow on L_α and L_3 phase-separating system can be summarized by using a shear diagram representing the different steady states as a function of temperature and shear rate (Fig. 5). In simple phase-separating Newtonian liquids, the interplay between viscosity, surface tension, and flow results in monodisperse spherical droplets whose size is shear dependent. This behavior is observed in our system at high temperatures (region III). On the other hand, at low temperatures the response of our system differs drastically. We observe large elongated droplets. Above a critical shear rate $\dot{\gamma}_c$ these droplets break to form a colloidal crystal of small monodisperse droplets whose size is almost independent of shear rate. This extraordinary behavior is likely related to the fact that this lamellar phase alone is able to form a crystalline structure at high shear rates as shown by Roux *et al.* [17]. A structural change of the L_α phase affects the viscosity and viscoelasticity difference between the two coexisting phases. The L_α phase is Newtonian at low shear rates and non-Newtonian for higher shear rates, above a few s^{1} [15]. In the high-temperature region of the shear diagram, most of the deformation is localized in the sponge phase domains because the viscosity of the L_3 phase is lower than that of the L_α phase and its volume fraction is much higher. The deformation supported by the lamellar domains is so low that this phase presents a Newtonian behavior. Therefore the two phase mixture results in this region to monodisperse droplets, similarly to phase separating Newtonian liquids. However, when the volume fraction of the L_α phase becomes more important, i.e., at low temperature in the shear diagram, the shear rate supported by the lamellar domains increases and drives this phase to its non-Newtonian regime. The lamellar phase undergoes then a structural change under shear leading to the formation of a crystal of onions. However, in contrast to the findings by Roux *et al.* [17] in a single phase lamellar system, the onion size in our case is shear-independent probably due to the presence of the sponge phase. In addition and contrary to single-phase lamellar system where the onion volume fraction is always 100%, the onion volume fraction can be continuously changed from 0 to 100 % by simply varying the lamellar phase volume fraction in the two-phase mixture.

For a two-phase system in which one of the coexisting phases exhibits strong structural changes under flow (as for the L_α phase), the domains organization of the two phases strongly depends on the shear-induced structural changes in this phase as shown in our study by the transition between the disordered droplets and the colloidal crystal. Finally as for single phase flow, the shear-induced structural changes occur through dynamic transitions and may lead to a structural bistability of the two-phase system.

We thank J.P. Delville, F. Nallet, and D. Roux for many fruitful discussions and T. Douar and M. Winckert for technical assistance. This work was supported by grants (PICS No. 610) and Région Aquitaine (CTP No. 980209202).

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