Coupling between Flow and Structure for a Lamellar Surfactant Phase

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The flow-structure relation of lamellar phases is studied using rheometry and cross-polarized microscopy under flow. The equilibrium phases show different defects. Low salinities lead to very viscous, "onion" phases, whereas at high salinity, a low viscosity plane lamellar phase is found. Under shear, the latter shows a sudden transition to a viscoelastic gel, with a texture and viscosity very similar to that of the onions. Gelation occurs after a certain delay time, increasing rapidly with salinity, by the nucleation of onions. This allows one to relate the delay time to the defect energy.

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During the past few years, the influence of shear flow on complex fluids has attracted much attention from both a theoretical and an experimental point of view [1–5]. Because large length and time scales are present in complex fluids (solutions of polymers or surfactants, for example), their organization may be affected by the flow field. This, in turn, may alter their rheological properties, which are of key importance for a number of applications. For these reasons, the study of the interrelation between flow and structure has received a lot of attention. Much studied are self-assembled surfactant systems, for which structural changes in the molecular assemblies induced by the shear have been reported [1–5]. For instance, transitions have been reported from "sponge phases" consisting of a bicontinuous isotropic network of multiconnected membranes, to lamellar phases, in which flat bilayers are stacked upon each other [2]. To understand how and under what conditions such "dynamical transitions" take place may teach us something about the nonequilibrium properties of such complex systems. Theoretical efforts have therefore attempted to model and predict the coupling between the flow field and the structure [6].

In this Letter, we relate the probability for the occurrence of a flow-induced transition to the equilibrium properties of the phases. We reveal a very sudden transition that occurs when lamellar phases are sheared. The transition leads to the formation of a very viscous gel containing onions, i.e., concentric stacks of bilayers in a lamellar matrix [3,4]. These are present also in equilibrium, but under different physicochemical conditions. We find that the further one moves away in the phase diagram from the equilibrium onion phase, the more time it takes to reach the gel phase. Both the equilibrium phase behavior and the probability for observing the transition can subsequently be related to the elastic constants of the surfactant bilayers.

We study [7] lamellar phases formed in aqueous solutions of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) at a surfactant concentration of 7% by weight, thus ensuring a constant amount of bilayers in the solution. A cut through the equilibrium phase diagram [8] at variable salinity (NaCl) shows a sequence of phase transitions that is usual for ionic surfactants. For low salinities, a lamellar phase is found. Increasing the salinity, first a coexistence between lamellar and sponge phases is found, after which (at even higher salinities) only the sponge phase remains.

Such changes of the topology of the bilayers are usually explained by considering the elastic moduli of the membranes. The equilibrium structures are governed by the membrane elastic constants and are obtained by minimizing the elastic energy [9]:

$$E = \frac{1}{2}\,k\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 + \bar{k}\left(\frac{1}{R_1 R_2}\right),$$

where R_1 and R_2 are the principal radii of curvature of the membranes; k and $\bar{k}$ are the elastic constants called the bending rigidity and the saddle-splay modulus. Experiment shows that, for the AOT system, k is unaffected by the addition of salt, and is of the order of $k_B T$ [10]; $\bar{k}$, on the other hand, is affected by salt, which changes the repulsion between the surfactant headgroups through a change in the Debye screening length. If $\bar{k}$ approaches zero from below upon addition of salt, the elastic energy will favor the lamellar phases at low and sponge phases at high salt.

This agrees with the phase diagram; however, a peculiarity of the AOT system is that for the lowest salinities (from 0 to 0.9 wt % NaCl), the lamellar phase is not constituted of periodically stacked planar bilayers, but forms spherulites, also called "onions" [11,12]. This observation is not in disagreement with the considerations for the elastic energy given above; if $\bar{k}$ is negative and dominates over the bending rigidity, the formation of spherical structures may be anticipated. The "onion phase" behaves like a gel: it is highly viscous and turbid and responds elastically to rapid deformations. Polarized microscopy indeed shows onion defects of different sizes, ranging from a few μm to a few tens of μm [visible as focal conic domains (FCD) II [13]]. These are equilibrium structures embedded in the lamellar matrix as concluded from electron microscopy [14]. The usual lamellar phase is found at higher salt (0.9 to 1.5 wt % NaCl). Microscopy shows oily streaks in a black homeotropic background (FCD I [13]).

The rheology on these phases is done on a Reologica Stress-Tech rheometer in a Couette cell with a gap of 1 mm. The cell is always filled very slowly, in order to minimize preshearing, and with the same volume so that the meniscus always coincides with the top of the inner and outer cylinder of the Couette cell. The inner rotating cylinder is cone shaped at its lower end, with a cone angle that ensures a constant shear rate everywhere in the cell. Evaporation was minimized by putting a cover on top of the Couette cell. The outer cylinder was thermostated at 20.0 ± 0.1 °C using a thermostat bath.

Figure 1 shows the viscosity as a function of time for the flat lamellar phase at different salinities for a fixed shear rate. We observe a sudden and sharp increase of η for each sample, of more than 2 orders of magnitude, which occurs at very different times for different salinities. At the viscosity maximum, a turbid and viscoelastic gel forms which is partially expelled from the Couette cell.

If we define the gel time t_g as the time for which the maximum value of the viscosity is reached, Fig. 2 shows the very strong dependence of t_g on salinity: an increase of 3 orders of magnitude over the small salinity range for which the lamellar phase is observed. For salinities lower than these, the onion phase is found, which is already gel-like. Thus, when one moves away from this phase in the phase diagram, the time necessary to form the gel increases roughly exponentially.

Measurement of the viscosity as a function of the shear rate shows that the new shear-induced phase has rheological properties that are very similar to those of the equilibrium onion phase (Fig. 3), whereas the viscosity of the plane lamellar phase is 2 orders of magnitude lower. This justifies the choice of t_g as the time of the viscosity maximum. Although at this point the solution is partially expelled from the Couette cell, it is unlikely that the viscosity increases beyond the value for the equilibrium onion phase.

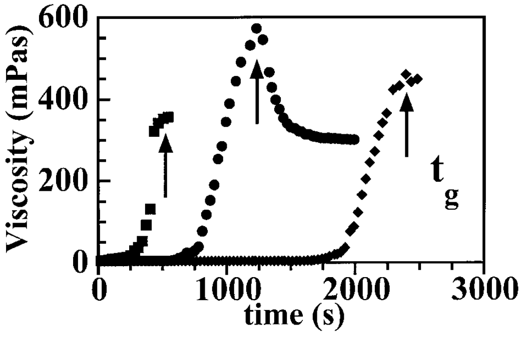

FIG. 1. Shear-induced formation of a gel phase after a delay time. Shown is the viscosity as a function of time when for a constant shear rate of 50 s^{-1} and for different salinities. Rectangles: 1.30 wt % salt; circles: 1.35 wt % salt; diamonds: 1.40 wt % salt. The arrow defines the gel time t_g for which the viscosity is maximum and the solution is partially expelled from the Couette cell.

To visualize the defects formed due to the flow, a transparent cone (angle 4°) and plate radius 60 mm) geometry is used that can be mounted directly under a polarized microscope. Figure 4 shows the images obtained during and after formation of the gel phase, revealing the presence of onions in a birefringent lamellar matrix. Electron microscopy [14] and polarized microscopy on the equilibrium onion phase indicate a texture of onion defects embedded in lamellae, so that the onions are connected by a network of bilayers, which is consistent with the microscopy observations presented here. We thus conclude, also from the rheology data, that the shear-induced gel formed out of the high-salinity lamellar phase is very similar to the equilibrium onion phase found at low salinities. In addition, Keller *et al.* [15] report a similar equilibrium structure for a very different (mixed) surfactant system; also here a gel was found. It consequently seems plausible that an onion texture in which different onions share a certain number of bilayers accounts for the high viscosity of these phases.

To account for the observed delay for formation of the gel, it is important to note that for a given salinity and shear rate, only small fluctuations around a mean value are observed. This is not what would be expected if the gel formation were due to a single random (activated) process. Performing a large number of experiments under exactly the same experimental conditions we obtain the distribution of gel times t_g (Fig. 2 inset). We obtain a peaked distribution, centered around a well-defined mean value away from zero.

Considering a single activated process, the probability P of nucleating the new phase is proportional to the nucleation rate. For an activation energy E_a, the nucleation rate is $\Gamma = \Gamma_0 e^{-E_a/k_B T}$ [16], with Γ_0 a characteristic attempt

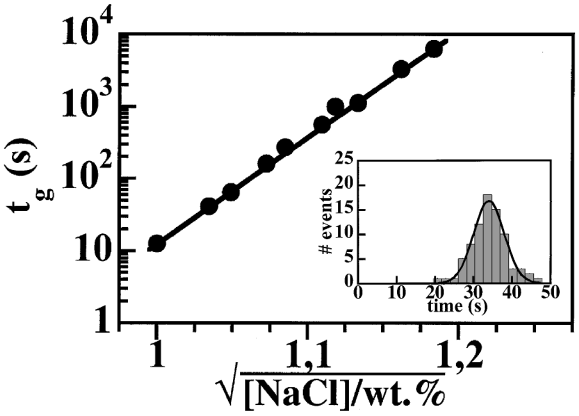

FIG. 2. Gel time t_g as a function of the square root of the brine salinity for a shear rate of 50 s^{-1}. The solid line is a fit that is explained in the text. Inset: distribution of gel times for 80 experiments at a shear rate of 200 s^{-1} and salinity (1.15% [NaCl]). The continuous curve is a Gaussian fit to the data.

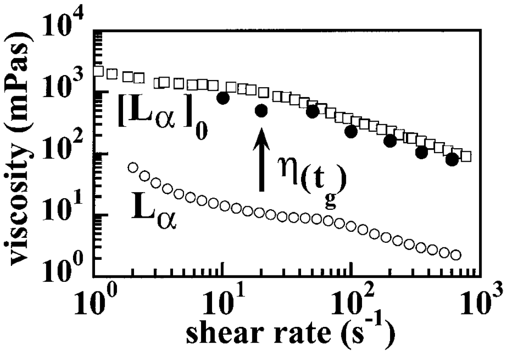

FIG. 3. Viscosity as a function of the shear rate. Lamellar phase: open circles are measurements before t_g and closed circles are the viscosity values at t_g. These are very similar to the equilibrium onion phase at low salinities (rectangles).

frequency, k_B Boltzmann's constant, and T the temperature. If the formation of the gel phase follows such a law, one would expect a Poisson distribution characterized by a single exponential decrease, which is not what is observed experimentally. If, however, one has a large number N of independent random events, each given by a Poisson process, one obtains [17] a peaked distribution away from zero, as is observed in the experiment.

For N independent random events each taken from a Poisson distribution, one finds for P:

$$P = \Gamma N(1 - e^{-\Gamma t})^{N-1} e^{-\Gamma t}.$$

The maximum of this distribution, corresponding to the average waiting time in the experiment, occurs for

$$t_{\max} = \frac{\ln(N)}{\Gamma_0} e^{E_a/k_B T},$$

and is thus found to still depend exponentially on the activation energy. The distribution is then exponential for $N = 1$, and close to a Gaussian for large N. In this, the ratio of the mean value to the width of the distribution equals $\frac{\ln(N)}{e}$. From the measured distributions, we find that this ratio varies between 3.4 and 6.8, corresponding to a large number of random events: $10^4 < N < 10^8$. Within the experimental uncertainty, N is found to be independent of both the salinity and the shear rate.

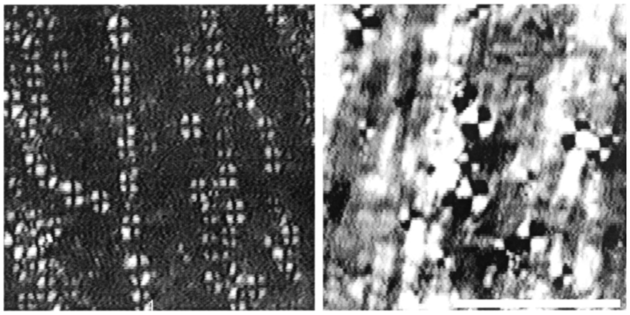

FIG. 4. Cross-polarized microscopy image taken under flow in the transparent cone-plate cell of the gel phase (a) just before t_g and (b) at t_g showing the onions in the lamellar matrix. The bar represents 100 μm.

Supposing that one such event corresponds to the formation of a single onion, we can compare with the number of onions observed. From the microscopy images taken just before t_g, we evaluate the maximum number of onions per image at around 1000. Taking a field depth of 60 μm, the maximum total number of onions is found to be of the order of 10^9, i.e., $\frac{\ln(N)}{e} \approx 7.7$. This value is of the same order, although somewhat larger than the one from the probability distribution. The experimentally observed distribution is thus close to but somewhat wider than the one obtained from the visualization. This might be due to slight variations in the initial conditions for the experiments; small changes in preparation (preshear) could account for the widening of the experimental distribution.

The activation energy for the formation of the onions can be obtained from the membrane elastic energy given above. The energy cost for the creation of a spherical vesicle (consisting of one closed surfactant bilayer) from a flat lamellar bilayer, is given by [9]:

$$E_{\text{sphere}} = 4\pi(2k + \bar{k}).$$

As already mentioned above, only $\bar{k}$ is expected to show a significant dependence on salt. It has been shown [14,18] that there are two contributions to $\bar{k}$: one originating from the aliphatic chains of the surfactant, and one originating from the electrostatic contribution of the counterions present in the solution. The former is supposedly constant as we vary only the amount of salt [14], whereas the latter varies as the square root of the salinity [18].

The final conclusion is then that, if the activation energy E_{act} can be taken to be proportional to the energy E_{sphere} necessary to create a *single* onion defect, the gel time t_g should vary exponentially with the square root of the brine salinity. This is in excellent agreement with the data (Fig. 2), although it should be noted that the salinity window is so small that it is difficult to distinguish between a square root and, for instance, a linear dependence. The arguments given here give in any case a plausible explanation for the extremely strong dependence of the gel time on the brine salinity.

In order to make a quantitative comparison, one needs values for the bending rigidity and the saddle-splay modulus. Such values were deduced [14] from electron microscopy observations. Although these are for more concentrated (15 wt %) AOT solutions, they should still be of the same order of magnitude in our system. For high salt, a variation $(2k + \bar{k})/k_B T \approx -0.2 + 0.3\sqrt{[\text{NaCl}]}$ is found. If this variation is used to account quantitatively for our results for the gel time, a good description of the data (the drawn line in Fig. 2) is found for $E_{\text{act}} \approx 10 E_{\text{sphere}}$, indicating that roughly 10 defects are formed in the process. Taking a typical distance between membranes of about 300 Å, this leads to a typical initial onion size of 0.3 μm. The onions observed in the flow visualization are larger (typically tens of μm); these initial onions may then constitute the nucleus of formation of the large onions.

The physical picture for the gelation of the lamellar phase is then that onions form in the flow field, at a rate that is limited by the elastic energy cost of forming such defects. The microscopy observations reveal that a long time before the macroscopic gelation, onions can already be observed in the flow. These onions are imbedded in the flat lamellar phase. They appear to be interconnected as they are observed to align in the flow [Fig. 4(a)]. If a very large number of onions are formed, the system becomes completely interconnected and is observed to gel macroscopically; the gel has a very large and anisotropic birefringence [Fig. 4(b)]. These observations account for the rheology observations that the viscosity increases slightly before jumping to a large value at the gel time.

In conclusion, we report a shear induced transition from a low-viscosity flat lamellar phase to a high-viscosity gel that contains onions [19]. In the equilibrium phase diagram, such a gel is present for low salinities. Increasing the salinity, the time necessary to form the gel from the flat lamellar phase under flow increases dramatically. This time should consequently be related to the elastic membrane energy necessary to create the defects. A simple model of a sequence of random activated processes indeed allows one to relate the flow-induced texture to the membrane elastic constants. This is, to our knowledge, the first time that such a direct flow-structure relation has been reported.

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