Large Deformations of Giant Floppy Vesicles in Shear Flow

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The flow deformation and rheology of vesicles of a soluble surfactant are studied. Direct observation under shear flow reveals that the vesicles become strongly elongated to form an entangled structure of connected bilayer tubes. The large deformation is due to the permeability of the membrane and the large solubility of the surfactant. The formation of the entangled structure is observed in the rheology as a strong increase of the viscosity with time. [S0031-9007(98)07534-6]

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Vesicles are closed membranes consisting of surfactant bilayers and have been intensively studied as model systems for biological cells [1]. More recently, the problem of the deformation of vesicles in hydrodynamic flows has been considered [2–6]. From a fundamental point of view, this is an interesting problem since both the surface area of the vesicle and its interior volume are usually supposed to be fixed [5,6]: The response to flow is then attributed to a dynamic surface tension. There is also a biological motive for understanding vesicle deformation in flow. One example is that of red blood cells, which are also vesicular structures. These have the capacity to pass through capillaries that are smaller than their own diameter, due to the deformation they undergo in the flow [7].

The flexibility or "floppiness" of vesicles at rest is determined by their bending rigidity κ, through the persistence length ξ of the membrane: $\xi = a \exp(2\pi\kappa/k_BT)$, with a a molecular length, k_B Boltzmann's constant, and T temperature [8]. If $\kappa \gg k_BT$, ξ is large and the vesicle remains flat over large distances in the presence of thermal fluctuations. If $\kappa \ll k_BT$, thermal fluctuations dominate, and the vesicle will appear very "floppy."

In a dynamical situation, for instance, under flow, if the total volume within the vesicle does not change, conservation of the number of surfactant molecules in the membrane (conserved surface area) leads to a dynamic "effective" surface tension σ_e, which also contributes to the response of a vesicle in a flow field [5,6].

Model vesicles are usually prepared from phospholipids, practically insoluble surfactants. A recent detailed study of the flow deformation shows that it is in general very small, and that even for high shear rates ($\approx 18\ s^{-1}$), the ratio of long and short axes of the vesicles $L/S \approx 1.3$: No large deformations are observed [4]. The deformation could be well described using the fixed area and volume constraints, allowing for evaluation of κ and σ_e [4]. The two constraints thus lead to small deformations [4–6], accompanied by a "tank treading" motion, in which the membrane revolves around the vesicle interior [3,4].

In this Letter we report extremely large deformations ($L/S \gg 100$) for vesicles that form spontaneously [9] in solutions of a soluble surfactant, even for very weak shear ($\approx 0.5\ s^{-1}$). Moreover, κ for these vesicles is similar to that of phospholipid vesicles [4]: both are on the order of a few k_BT. The large deformation entails the formation of very long and thin, filamentlike bilayer structures that are interconnected and form a highly entangled microstructure. The formation of these entangled structures leads to a dramatic antithixotropic behavior: under constant shear, the viscosity of the solution increases in time by up to 2 orders of magnitude. Some similarities are observed with the behavior of wormlike micelles, for which an entangled structure is already present in equilibrium [10].

Solutions of the anionic surfactant AOT (sodium bis octyl sulfosuccinate) are prepared by dissolving AOT and NaCl in ultrapure water [9]. A striking milky-white color reveals the presence of micron-sized objects in the solution. Phase-contrast microscopy [Fig. 1(a)] shows that just above the critical micellar concentration (cmc), large aggregates made up of surfactant bilayers appear in the solution [9]. Additionally, cryo-transmission electron microscopy (cryo-TEM) experiments show no micelles and a very low concentration of vesicles on length scales between 50 Å and 0.5 μm. Although spherical micelles may be too small to be detected in the Cryo-TEM experiment, it appears unlikely that a coexistence between three different surfactant structures (monomers, micelles, and vesicles) could be observed: The system is thus observed to form very large aggregates rather than micelles.

Vesicles exist with different numbers of bilayers [9], which shows up as the difference in contrast between the contours of different vesicles and measurements of the bending rigidity of these vesicles. κ is determined from the equilibrium distribution of thermally excited bending fluctuations of tubular vesicles [11]. The lowest value for κ we found in this way is $(8 \pm 2)k_BT$, but also multiples of this value were found, thus corroborating the microscopy observations that the vesicles are multilamellar.

The rheology was done on a Reologica Stress-Tech rheometer, in a Couette geometry. Figure 2 shows the evolution of the viscosity of the solution with time. The unsheared solution has practically the viscosity of water

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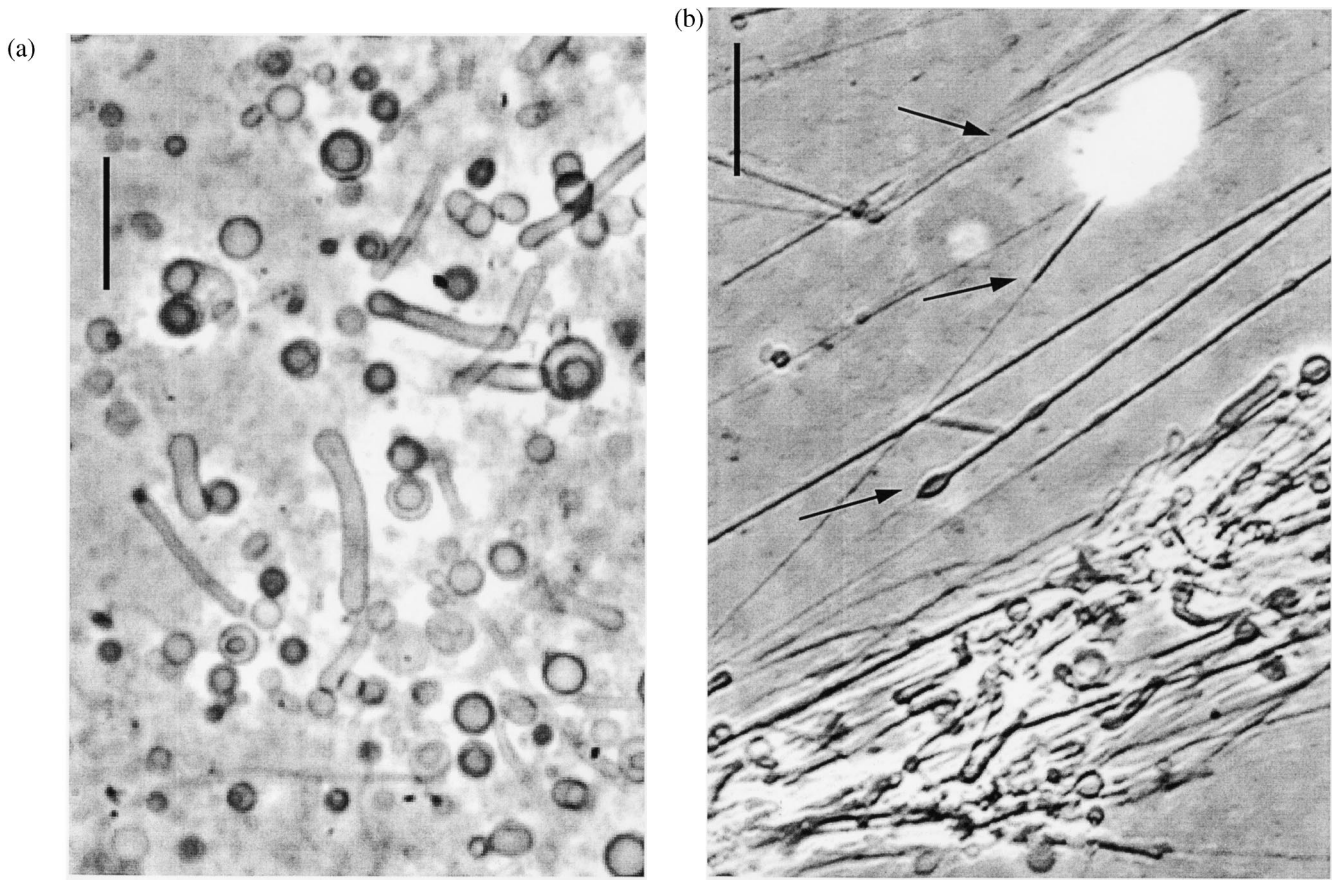

FIG. 1. Phase-contrast micrographs of a 7.6 mM AOT solution at [NaCl] = 0.075 M; (a) at rest, spherical as well as tubular vesicles are observed; (b) under a continuous shear flow of 0.5 s^{-1} very long and thin filamentary bilayer tubes are observed, forming an entangled structure. The tubes appear to be under tension since they are stretched in the flow field. Arrows indicate transitions from thick to thin filaments. Bars are 30 μm.

(1 mPa s), as the surfactant solution is very dilute. In time, a very steep rise of the viscosity η is observed up to a maximum, after which η decreases again to settle at a plateau that is still very much larger than 1 mPa s. For high shear, the maximum disappears and only the pronounced antithixotropic behavior remains.

The cause of the antithixotropy becomes evidently clear when observing the solution under shear directly under the phase-contrast microscope. For this purpose, we constructed a plate-plate shear cell, consisting of two glass disks, separated by a thin (0.25 mm) spacer, the upper disk rotating [12]. Figure 1(b) shows the strong deformation of the vesicles into very long and thin filamentlike bilayer tubes, mostly oriented in the flow direction. A highly entangled structure is observed, with a large number of connections between the filaments, as in a spider's web, which accounts for the viscosity increase. Also, the solution becomes very inhomogeneous: The filaments can be organized in bundles, with little or no visible structures between them. Larger objects form in the flow, from which again bilayer tubes form, which, in turn, are stretched in the flow field; this process appears to continue indefinitely. A dynamical equilibrium between stretching and recoiling of the tubes is reached, which accounts for the leveling off of the viscosity at a plateau value.

In order to define a characteristic time for the response of the system to the applied shear, we note that all the transient rheological properties are simple exponential functions of time with a single characteristic time τ. Figure 2 shows an exponential fit to the viscosity increase after the onset of flow. Figure 3 demonstrates the exponential relaxation of the viscosity after the cessation of flow at the viscosity plateau, with the same τ as that for the rise. The characteristic times for the rise and the descent of the viscosity (if a peak is present) under continuous shear are also the same (Fig. 4). Thus, all these processes can then be described by a single τ.

Measurements as a function of surfactant concentration show that, above the cmc, the plateau value for the viscosity increases linearly with the surfactant concentration C over the domain cmc $< C <$ 9 mM. The relaxation time for a given shear rate, on the other hand, is independent of surfactant concentration over this range [13]. The relaxation time does, however, depend on the shear rate. Figure 4 shows that τ decreases as a power law of the shear rate, with a power of -0.8 ± 0.2. Likely, the

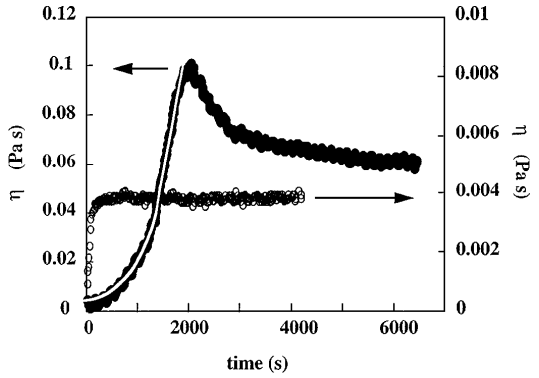

FIG. 2. Viscosity of the solution shown in Fig. 1 as a function of time. For low (closed symbols, 0.5 s^{-1}) and high (open symbols, 30 s^{-1}) shear. The white line is a fit to an exponential increase, yielding τ.

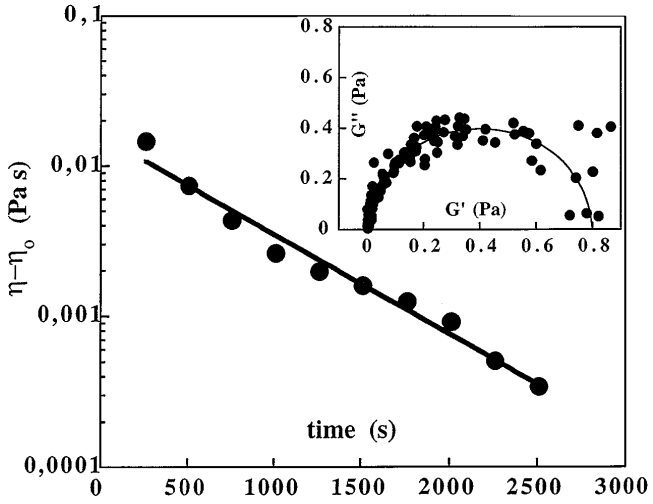

FIG. 3. Stress relaxation after the cessation of flow for a 9 mM sample presheared until the viscosity plateau. Inset: G'' vs G' for the same solution, presheared in the same way. The semicircle is the expected result when only one relaxation time is present in the system.

shear rate dependence of τ can be attributed to a change in entanglement. The change in entanglement is also compatible with the shear rate dependence of the viscosity plateau η (Fig. 4). Also here, power-law behavior is found, the power being equal to that found for τ: -0.8 ± 0.2.

The elasticity of the entangled structure formed under shear is evident from the observation of a very large recoverable strain upon cessation of flow. If one stops the experiment at the viscosity plateau, the inner cylinder of the Couette cell starts to turn in the opposite direction, typically 2π radians. The recoverable strain, defined as the distance traveled by the inner cylinder relative to the gap of the Couette cell, for instance, for a 7.6 mM AOT solution presheared at 1 s^{-1}, is 8000%; for other preshear rates also several thousands of percents are found.

The viscoelasticity of the entangled microstructure can be determined because of the very slow stress relaxation (minutes to several tens of minutes; this also allows for the cryo-TEM observations for which the sample preparation time is 3 min). These measurements are difficult because of the relatively low viscosity and elasticity of the solution (compared to systems usually studied in rheology). Although the relaxation is slow, the system does evolve during the measurements. For this reason, these were performed from high frequencies (for which the measurements can be done rapidly) to low ones. In Fig. 3, we show the result: the viscous (loss) modulus as a function of the elastic (storage) modulus for different frequencies. The observation that the data roughly fall on a semicircle implies that there is again only one characteristic relaxation time in the system (for a given preshear rate) which describes the crossover between viscous behavior at low frequencies to elastic behavior at high frequencies.

The results for the viscosity of the vesicular phase bear some similarity to those for wormlike micelles under a continuous shear flow. There are two main differences with our system. First, for the micelles system, a dynamical network is already present in equilibrium [14]. Second, for the unsheared micelles, the tubelike structures are very thin cylindrical micelles, constituted of a single monolayer, so that the length scales involved for the micellar system are much smaller. In spite of these differences, the behavior of the viscosity as a function of time is similar to that observed for the micelles [10(a)]. Also, measurements by Rehage and Hoffmann and Clausen *et al.* [10(a)] report a power of -0.89 ± 0.13 for the shear rate dependence of the viscosity, whereas we find a power of -0.8 ± 0.2. Another important point is that recent freeze-fracture electron microscopy observations on sheared wormlike micelles [15] reveal the existence of large inhomogeneities also for the micellar system, similar to our microscopy observations under flow [Fig. 1(b)]. Cryo-TEM observation of our sheared vesicular solution, on the other hand, does not provide much new information: All along the viscosity vs time curve, we observe the existence of a few, mostly unilamellar, vesicles [13]. Thus, under continuous shear, the two systems behave similarly, only on a different length scale.

Recently, shear-induced transitions from a vesicular to a wormlike micelle phase were reported in a system for which these two phases are very close to each other in the phase diagram [16]. This is unlikely to happen for our system, as (i) microscopy observations show that the entangled structure is formed of bilayer, rather than monolayer tubes, (ii) the AOT system does not form cylindrical micelles in equilibrium [9], and (iii) cryo-TEM observations do not show the presence of wormlike micelles.

Chiruvolu *et al.* [17] recently discovered an equilibrium entangled tubular vesicle phase for an insoluble surfactant (a phospholipid) in the presence of a cosurfactant. The bending rigidity of these tubular vesicles was determined to be about $2k_BT$, comparable to that of the AOT vesicles. Between the two systems, the absolute values of the viscosity are difficult to compare, as the data of Ref. [17]

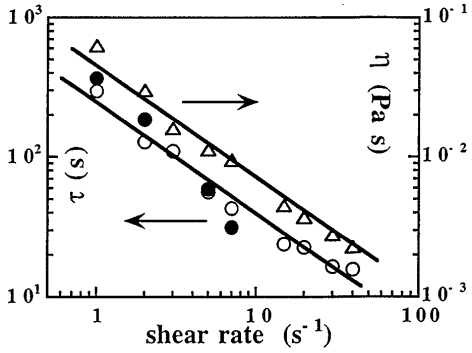

FIG. 4. Relaxation time τ (closed circles: viscosity rise; open circles: viscosity decrease) and plateau value of the viscosity (triangles) as a function of the applied shear rate.

are for a solution that is very concentrated compared to ours. The striking difference between the phospholipid and the AOT vesicles is that the steady-state viscosity of the equilibrium tubular vesicle phase hardly shows any dependence on the shear rate, whereas we report a pronounced decrease of the plateau value for the viscosity. The cause of this difference should be sought in the relative ease with which the AOT vesicles are deformed by the flow field [13].

The large deformation of the AOT vesicles is contrary to what is found for the spherical phospholipid vesicles [4]. The differences between the two systems are that (i) in a previous experiment on the AOT vesicles, we observed the large permeability of the membrane to water [9]. This implies that pressure differences between the interior and the exterior can easily be equilibrated. It is therefore unlikely that the volume conservation constraint is satisfied; (ii) compared to the phospholipid vesicles, a large amount of surfactant monomers is present in solution for the AOT system. This implies that new surfactant can be embedded in the membrane as soon as it is stretched in the flow and that, consequently, also the area constraint is unlikely to be satisfied.

The importance of the presence of surfactant monomers in the bulk of the system can be demonstrated as follows. The cmc of AOT, which gives the amount of free monomers in solution, varies with the brine salinity. We thus prepared solutions with a different cmc, but exactly the same amount of AOT in vesicles (3.2 mM). Comparing the plateau value of the viscosity for these different solutions, it is found to decrease linearly with the amount of AOT monomers in the salinity range between 0.02 and 0.08 M NaCl. The effect of the free monomers on the floppiness of isolated vesicles can in principle be incorporated in the existing models for vesicle deformations as an additional contribution to the dynamic surface tension. This tension will be lowered considerably if surfactant molecules can arrive from the bulk [18], leading to more floppy vesicles than those made of surfactants with a low solubility.

The membrane permeability, on the other hand, is impossible to incorporate in the models, as the very starting point of these is the conservation of volume within the vesicle interior. It is also very clear that the permeability contributes to the floppiness of the vesicles observed in our experiment. This is corroborated by a recent Monte Carlo simulation of floppy vesicles in flow [2]. Without the constraint of volume conservation, the simulated vesicles also show deformations that are comparable to the ones observed here, and even the very elongated filament-like structures can be observed in the simulations [2].

LPS de L'ENS is URA 1306 of the CNRS, associated with universities P6 and P7.

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