Time-Resolved Small-Angle Neutron Scattering Study of Shear-Thickening Surfactant Solutions after the Cessation of Flow

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Shear effects in dilute solutions of gemini surfactant solutions are studied by SANS in the shear-thickening regime. After the cessation of flow, the local anisotropy relaxes in about 10^2 s and we find evidence for a shear-induced change in the structure of the solutions that is stable for at least a few hours. The results can be understood if the shear-induced viscous phase is a loosely connected network of long-lived aggregates with typical size of 1 μm. Counterions-mediated attraction between rodlike micelles could explain the formation of the aggregates and their long lifetime. The whole picture is consistent with previous results obtained for the same system using different techniques.

Introduction

A number of dilute ionic surfactant solutions exhibit an increase of their steady-state viscosity by a factor up to 20−30 when they are sheared above a critical shear rate value $\dot{\gamma}_c$. This increase occurs after an induction time that decreases as the shear rate $\dot{\gamma}$ increases beyond $\dot{\gamma}_c$ and that can be as long as several minutes for $\dot{\gamma}$ close to $\dot{\gamma}_c$. This intriguing shear-thickening behavior has raised much interest since its discovery in the early 1980s[1−17] and has been studied by different experimental techniques including strain and stress controlled rheology,[1,3,4,6−10,12−15] flow birefringence,[4,14] flow electrical conductivity,[14] cryo-TEM,[14] freeze-fracture electron microscopy,[15] light scattering microscopy,[10,12,13,16] light scattering,[11] or small-angle neutron scattering.[2,5,7,8,17] The current emerging picture favors a shear-induced separation of the fluid into one highly viscous ("gellike") and orientated phase and one phase still containing small isolated rodlike micelles. However divergent views still persist concerning the nature of this transition.

Pine et al. have shown[10,12,13,16] that the control parameter of the steady-state behavior is the shear stress rather than the shear rate. Under controlled shear stress conditions, the reported behavior bears features similar to a first-order phase transition like in liquid−gas transition. The induction time would then correspond to a latency time for the nucleation of the highly viscous phase.

On the other hand, other authors[11,14] conclude or suggest that micelles aggregation occurs already at smaller shear rates than $\dot{\gamma}_c$ and that the shear-thickening occurs once the mean size of the aggregates has reached some critical value. This idea is supported by the fact that $\dot{\gamma}_c$, the induction time, and the time to reach the steady state appear to vary with the gap size of the shear cell.[9,14] The induction time would then be related to a growth rate of the micelles controlled by the hydrodynamics.

Current models[18−21] have considered a growth mechanism involving the collinear fusion of micelles aligned in the flow. However the predicted $\dot{\gamma}_c$ values are orders of magnitude larger than the experimental values, likely due to the fact that interactions between the micelles are not taken into account in these models. In fact we are still lacking any idea about the microscopic nature of the viscous phase and several studies have pointed out the possibility that the flow could couple energetically close phases in the phase diagram of these systems.[14,17] This could explain that times much longer than any viscoelastic times are usually needed for the systems to recover their initial low zero-shear viscosity after the cessation of flow.

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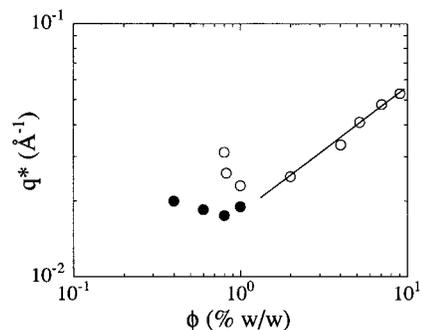
In this paper, we report first evidence for a change of the microstructure of dilute surfactant solutions under shear flow in the shear-thickening regime. By using small-angle neutron scattering (SANS), we have been able to observe a shift of the correlation peak in the sheared solutions and an increase of the scattering intensity at small scattering wavevectors. These modifications are only observed for solutions below the overlap concentration and are stable for at least a few hours after the cessation of shear. In contrast, the anisotropy of the solutions decays on much shorter times of the order of 100 s that are almost still 1 order of magnitude larger than the characteristic time for the decay of the macroscopic anisotropy, as measured by flow birefringence. Our results suggest an inhomogeneous structure of the viscous phase involving locally long-lived (possibly metastable) structures connected at larger length scales by more labile structures.

Experimental Section

We have used a dimeric surfactant, the ethanediyl-1,2-bis(dodecyldimethylammonium bromide),[22] hereafter called $12-2-12$, synthesized in our laboratory. Solutions are prepared by weighing the surfactant molecules in D_2O. They are stirred at 50 °C for a few hours to ensure a complete dissolution and then filtered through 0.2 μm filters.

Small-angle neutron scattering experiments were performed on spectrometers PAXY (Laboratoire Léon Brillouin, Saclay, France) and D11 (Institut Laue Langevin, Grenoble, France). Temperature has been kept to 20 °C through all of the experiments. The shear flow was generated in a Couette geometry (concentric cylinders),[23,24] the incident beam being parallel to the velocity gradient. The two-dimensional detector thus measures the scattering intensity for wave vectors **q** in the plane perpendicular to the velocity gradient. Scattering wave vectors are then defined by their amplitude $q = 4\pi/\lambda \sin(\theta/2)$, λ being the incident wavelength and θ the scattering angle, and their azimuthal angle ψ, $\psi = 0°$ corresponding to the direction parallel to the flow. The q range covered in these experiments lies between 6×10^{-3} and 4.5×10^{-2} Å^{-1}, varying slightly for the three sets of experiments (2 sets on PAXY, 1 set on D11) performed for this study. Data treatment has been kept at the simplest level, involving only normalization by incident flux, sample transmission, and sample thickness, with no subtraction of the incoherent background. Nevertheless the large contrast of the surfactant molecules with respect to the solvent ensures large enough coherent scattering intensities to allow a superposition of the data in the high-q range when they are normalized by the concentration. Thus the level of incoherent background remains low for all our samples and does not influence our results. For anisotropic samples, standard procedures have been applied to average scattering intensities for each q value on azimuthal sectors with width $\Delta\psi = 15°$.

In the dilute concentration regime investigated here, the intensity scattered from the solutions is rather low. Thus very poor statistics are obtained for anisotropic spectra regrouped on narrow azimuthal sectors when the counting time is about 60 s, a typical duration in the time-resolved experiments. To achieve reasonably good statistics, it was therefore necessary to perform a large number of cycles involving steady shear followed by a rest sequence. The shear rate was chosen well above the concentration dependent critical shear rate $\dot{\gamma}_c$, and the shear flow was established for 600 s, a duration longer than the time needed to observe the steady-state rheological behavior in the conditions of these experiments.[14] Typically 15 spectra with short counting time were successively recorded while the flow was stopped. Spectra from different cycles but with corresponding delay time after the cessation of flow were then averaged azimuthally as described above and added together. Summation was performed first by groups of a few spectra (typically 10) to check for the absence of aging in the samples, especially

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Figure 1. Variation of SANS peak position with surfactant concentration: closed symbols, this work; open symbols, data from ref 8. The straight line corresponds to a slope $^{1}/_{2}$.

evaporation, by comparing different groups of data. In a few cases, the last group gave different averaged curves and was discarded. Finally all the groups were summed together. The total number of cycles was between 25 and 100, depending on the concentration of the samples, the time resolution, and the intensity of the neutron source.

Results

In the absence of salt and above the overlap concentration $\phi^* \approx 10^{-2}$ (w/w), the $12-2-12$ surfactant molecules assemble to form an entangled solution of flexible, wormlike micelles. The scattering intensity at rest is reminiscent of the intensity scattered from polyelectrolyte solutions and exhibits a correlation peak with a position q^* scaling as $\phi^{1/2}$.[7,8] However the shear-thickening behavior is observed close to the overlap concentration and mainly in the dilute regime ($\phi < \phi^*$), where q^* increases when decreasing the concentration (Figure 1).

As reported earlier for this system as well as for other surfactant systems, in the presence of a shear flow the amplitude of the correlation peak decreases along the direction parallel to the flow and increases along the direction perpendicular to the flow (along the neutral axis). For systems exhibiting shear-thickening behavior, this anisotropy appears only for shear rate values larger than the characteristic value $\dot{\gamma}_c$ corresponding to the increase of the steady-state viscosity, i.e., to the onset of shear-thickening. For the present system, $\dot{\gamma}_c$ increases strongly with temperature and is a decreasing function of concentration.[14] The first feature appears to be more general than the latter one.[17] It can be noted that the experimental values of $\dot{\gamma}_c$ are consistently smaller than the rotational relaxation rate,[14,17] in contradiction with the current available theories that assign the shear-thickening behavior to the collinear fusion of elongated micelles aligned by the flow.[18-21]

A feature that was overlooked in previous studies is the small shift of the correlation peak to smaller q values when a shear flow is applied. Although this phenomenon was visible in Figure 6 of ref 8, it was not discussed. It was however mentioned in ref 7. In fact it seems that this phenomenon becomes more pronounced as the concentration is decreased below ϕ^*. Figure 2 shows the effect of shear rate on the intensity scattered in the direction perpendicular to the flow for a sample with $\phi = 4 \times 10^{-3}$. In this case the shift of the maximum is associated with an increase of the scattering intensity in the small-q region. For higher concentrations, this increase is less pronounced. As far as we know, no shift of the peak position with shear flow was ever reported for surfactant solutions in the semidilute concentration range above ϕ^*,[2,5,17,25] where mostly shear-thinning behavior is observed.

After the cessation of flow, the anisotropy decreases rapidly. Figure 3 shows intensity data repeatedly
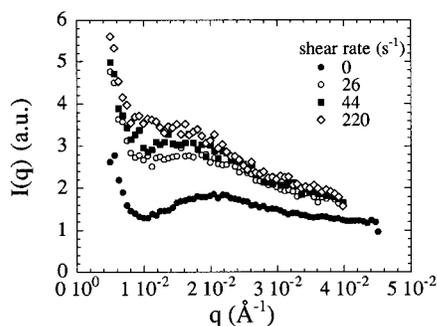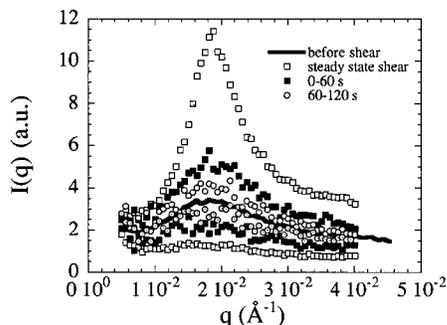
Figure 2. Evolution with shear rate of the SANS intensity in the direction perpendicular to the flow for a sample with $\phi = 4 \times 10^{-3}$ (w/w).

Figure 3. Evolution of the scattering intensity in the directions perpendicular (data above the isotropic state curve) and parallel (data below the isotropic state curves) to the flow after the cessation of shear ($\phi = 10^{-2}$). Numbers indicate the time delay window for data acquisition after the cessation of shear. Curves corresponding to the window 120–180 s are omitted for the sake of clarity but still display some anisotropy.

accumulated during short time intervals after the cessation of shear for a large number (25) of cycles consisting of steady shear ($\dot{\gamma} = 77$ s^{-1}) during 600 s followed by a period of rest (780 s). After a time of the order of 100 s, the intensity curves along the parallel and perpendicular directions are identical within experimental accuracy. For shorter times, the decay of the anisotropy compared to the one observed during the steady state of the shear flow is clearly visible. The time corresponding to the disappearance of the anisotropy is about 180 s for $\phi = 10^{-2}$, 60 s for $\phi = 6 \times 10^{-3}$, and 100 s for $\phi = 4 \times 10^{-3}$. However the time resolution of the present data is not fine enough to provide any definite conclusion on the variation of this time with concentration. Future experiments are planned for a more detailed investigation.

Strikingly, in the dilute regime investigated here, the isotropic state obtained after the relaxation of the shear-induced anisotropy does not correspond to the original isotropic state, i.e., before any shear flow has been applied to the samples. Figure 4 compares the intensities measured before any shear flow and after a few hours of rest for three different concentrations. In the latter conditions, the maximum of the intensity retains the position corresponding to the conditions of steady-state flow and some fraction of the intensity increase at small q values remains. On the other hand, our sample with $\phi = 10^{-2}$, which showed no shift of the peak position and no increase of the intensity scattered at small q values, has identical structure factors before and after the shear flow. The apparent discrepancy with the behavior shown in ref 8 can be explained by a slightly higher temperature in the latter experiment,
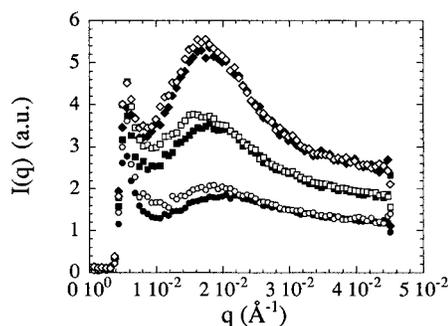
Figure 4. Comparison of SANS intensity curves measured before any applied shear flow (closed symbols) and after a long rest time T once the shear flow (220 s^{-1}) has been stopped (open symbols): circles, $\phi = 4 \times 10^{-3}$, $T = 160$ min; squares, $\phi = 6 \times 10^{-3}$, $T = 240$ min; diamonds, $\phi = 8 \times 10^{-3}$, $T = 55$ min. The acquisition time is 1000 s for each curve.

resulting in a shift of the overlap concentration to higher values. In fact, our sample with $\phi = 10^{-2}$ was measured at 20 °C and its peak position still obeys the characteristic $\phi^{1/2}$ power law of the semidilute regime, which is not the case for the $\phi = 10^{-2}$ sample in ref 8 (see Figure 1).

Discussion and Conclusions

The data in Figure 4 give strong evidence for the existence of a shear-induced structure that remains stable for times up to at least a few hours. One striking feature in shear-thickening surfactant solutions is the fact that, depending on the length scale probed by the measured quantity, the time scale characterizing the decay from the steady-state value, once the shear flow has been stopped, can differ by several orders of magnitude. Thus, for the present system, the flow birefringence decays in about 10 s [14] and the anisotropy measured by SANS decays in about 10^2 s, while some shear-induced features of the SANS intensity are stable for times larger than 10^3 s. The fact that this time scale increases as the probed length scale decreases rules out a single relaxation mechanism such as diffusion and points to the existence of several relaxation processes.

In fact inhomogeneous structure for the shear-induced viscous phase has been speculated before[26] and indeed has been observed by cryo-TEM[14] on 12–2–12 solutions. For the present system, such an inhomogeneous structure should relax rapidly on large macroscopic length scales, exhibit some anisotropy at the length scale probed by SANS technique, and contain long-lived parts. A possible shear-induced organization would thus consist of oriented anisotropic aggregates (possibly bundles of micelles) loosely connected in a 3-dimensional network by elongated wormlike micelles. Such a structure would relax the stress (i.e. flow birefringence) rapidly, on a time scale of a few seconds, typical of the rheology of wormlike micelles,[27] exhibit some structural anisotropy until the aggregates have randomized their orientation by diffusive rotation, and need a still longer time to dissolve the aggregates back to the original unsheared solution. In this picture, it is not clear whether the anisotropic structure of the aggregates results from a mere anisotropic growth in the flow or involves more complex pheomena. In fact, in the very same concentration regime where shear-thickening is observed,[14] an anomalous negative component in the electric birefringence was reported for the same system[28,29]

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and was interpreted as a possible indication for local orientational order of the rods in the solutions at rest.[30]

Recently considerable progress has been achieved in the understanding of short-range attractive electrostatic interactions between rodlike particles with the same net charge.[31−35] The condensation of small ions onto the rods gives rise to fluctuations in the local charge density that become correlated for close enough parallel charged cylinders. It has been shown that the resulting multipolar electrostatic interactions produce an effective short-range attractive interaction for two parallel rods bearing the same net charge.[31,32] For an assembly of rods at high enough concentration, the short-range attraction should then result in the growth of bundles of rods with infinite size and lead ultimately to phase separation.[34] However Ha and Liu have shown very recently[35] that the energy barrier to overcome for a rod to aggregate with an existing bundle of N rods increases as $N^{1/2}$ when the rod approaches the bundle in a noncollinear configuration. Thus, for kinetic reasons, there is a limiting size of the bundles obtained when the energy barrier is of the order of the thermal energy, since the approach of a rod with random alignment to a distance short enough to probe the attractive interaction becomes then very unlikely.[35]

Although micelles are not permanent objects, similar mechanisms could be present in solutions of rodlike micelles since charge fluctuations are much faster than both the intermicellar exchange of surfactant molecules and the breaking time of the elongated micelles. We could then expect the aggregation of parallel rodlike micelles into bundles. Furthermore the presence of flow would increase the probability of collinear configurations and favor an increase of the kinetically limited size of the aggregates. With this mechanism, the existence of an induction time for the shear-thickening behavior appears rather natural.

At that point, it can be remarked that the onset of attraction between like-charged rods has been found only in the presence of multivalent ions and that the range of the attractive force is very short (typically below 10 Å).[31−35] These features seem to exclude a priori the existence of such a mechanism in our case. However, SANS and SAXS studies show that our micelles have a radius about 20 Å and that more than 90% of the Br$^-$ are condensed in a very narrow skin of about 2 Å at the cylindrical surface.[36] Such a geometry has not been considered in the models up to now and could share some features with the situation of two like-charged planar surfaces. Indeed, in the case of rods interacting with a planar like-charged surface, attraction was found even in the presence of monovalent ions at high enough charge densities.[37] Moreover, most theoretical studies use a uniform charge density to quantify the charge on the rods before any condensation of the counterions takes place, while the maximal attractive force between a uniformly charged rod and a surface increases when the charges on the latter are discretized.[37] In the absence of any model suited to our experimental system, we do not want to comment further on the applicability of counterion-mediated attraction to explain the observed aggregation of our like-charged micelles and we leave this applicability as an open question.

Within the picture of loosely connected oriented aggregates, the anisotropy relaxation time measured in our SANS experiments would then correspond to a rotational diffusion time τ_R for the aggregates. If we approximate them as elongated structures with large aspect ratio, their typical length L would then be $L \sim (kT\tau_R/\eta)^{1/3} \approx 1.1~\mu$m, if η is taken as the solvent viscosity and $\tau_R \approx 10^2$ s. Although this order of magnitude for L compares very favorably with the results of cryo-TEM,[14] we must keep in mind that some size polydispersity of the aggregates is likely and that, moreover, the use of the solvent viscosity in this estimate might be erroneous. In fact, if a very low shear rate is applied to a solution that has reached the steady-state shear-thickening regime, the measured viscosity takes about 500 s at 20 °C to relax to its presheared value.[14] Thus large aggregates might experience a viscosity larger than the solvent viscosity[38] during their rotational motion. However, for our experimental conditions, there is at most a factor 10 between the solvent viscosity and the shear-thickened solution viscosity and the $^1/_3$ power law reduces drastically the influence of this hypothetical effect on the estimated L value, which remains altogether consistent with the cryo-TEM observations.

We now turn to the SANS intensity curves measured once the anisotropy has relaxed (Figure 4). At first thought, the presence of large aggregates could explain the increase in the intensity scattered at small q values while the decrease of bulk surfactant concentration due to the aggregation could be responsible for the shift of the correlation peak to smaller q values. However such a simplistic interpretation does not consider correctly the role of interactions between aggregates. In fact the height of the correlation peak and the intensity at vanishing q are also related to the correlation hole in the pair correlation function of aggregates and no definite conclusion can be made without separating intra- and intermolecular contributions of all the scattering species in solution. This very difficult problem is beyond the scope of this paper, and we stay with the experimental evidence for a long-lived shear-induced state of the solution, different from the state before shearing and probably consisting in a mixture of aggregates and short micelles.

The long lifetime of the aggregates appears very surprising for micellar solutions where intermicellar exchange of surfactant molecules and breaking/recombination of micelles are fast processes that are expected to facilitate the homogeneization of the solution once the shear flow is stopped. This apparent contradiction can be resolved if a counterion-mediated attraction is involved in the formation of the aggregates. For permanent rodlike molecules, this attraction results in the formation of stable bundles with infinite equilibrium size.[34,35] Similarly, aggregates of micelles can be expected to be stable if the same attraction is at work, with no trend to dissolution for an aggregate except for the two fast processes mentioned above. However their efficiency decreases as the size of the aggregates becomes larger. Inside one aggregate, the exchange of surfactant molecules is likely to occur mostly between the neighboring micelles forming the aggregate and should not contribute to its dissolution. When a micelle belonging to a bundle breaks, it cannot easily diffuse toward the bulk solution and there is a high probability for a local recombination. Thus both processes are efficient mechanisms of dissolution only for the borders

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of the aggregates. A rather large lifetime could then be related to the low surface-to-volume ratio for aggregates with typical size around 1 μm.

Although the above considerations are only conjectures (see above), it remains that the observed long-lived shear-induced state is consistent with rheology experiments reporting a relaxation of the viscosity occurring on time scales much larger than any usual rheological time in these systems. Also a long-lived structure can explain that, at the start of a steady shear rate step, the transient behavior before the achievement of steady state depends on the shear history of the sample.[39]

Although the proposed picture for the viscous shear-induced phase is consistent with the results of previous works reporting on the same system and in particular with cryo-TEM experiments, it appears rather different from the pictures obtained by freeze-fracture elctron microscopy on a different system.[15] Apart from the ever lasting debate about possible alteration of the structure involved in the preparation of samples suitable for electron microscopy, there remains the more fundamental and still open question whether the microscopic structure of the viscous phase, i.e., in the present case the aggregates, should be expected to bear some universal features, despite the fact that the phase diagrams of the investigated systems can differ considerably. The mechanism described above would certainly imply some common features between different surfactant systems, but we can also expect a number of different aggregation regimes de-

pending on parameters such as the nature of counterions, the degree of condensation, the ionic strength, or the length of the hydrophobic tails. The body of experimental results is yet to be enriched to obtain a general understanding.

To conclude, we report in this paper the first estimate for a local anisotropy relaxation time and the first evidence for a long-lived shear-induced structural change in shear-thickening dilute gemini surfactant solutions. The results can be understood if the shear-induced viscous phase is viewed as a weakly connected network of anisotropic aggregates, the links between the aggregates being much more labile than the aggregates themselves. This picture remains consistent with the previous results obtained by rheology, electrical conductivity, flow birefringence and cryo-TEM experiments on the same system. Its validity for other surfactant systems remains as yet an open question. Counterion-mediated attraction between the rodlike micelles appears as a possible mechanism to explain the formation of the aggregates and their stability. Experiments with divalent counterions are planned in the next future and should help to clarify the role of counterion-mediated attraction in the observed aggregation.

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