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The Study of Anisotropically Shaped Micelles Subjected to Shear Flow by Small-Angle Neutron Scattering[1]

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The development of Couette shear-flow cells for use with small-angle neutron scattering (SANS) has provided the opportunity for the morphology of solutions of anisotropically shaped surfactant micelles to be probed in more detail and for the effects of shear on such structures to be explored. The effects of finite concentration (hindered rotation and interactions), flexibility, and shear-induced changes/structures are described for elongated micelles in their dilute phase (for a range of ionic, nonionic, and mixed ionic–nonionic micelles). Some recent measurements on nonionic and mixed ionic–nonionic micelles demonstrate that SANS can provide a vital insight into the rheological properties and morphology of micellar solutions over a wider region of their complex phase diagrams.

KEY WORDS: Anisotropically shaped micelles; complex fluids; Couette shear flow; mixed surfactants; shear-induced structures.

1. INTRODUCTION

The development of Couette shear-flow cells [1, 2] for use with small-angle neutron scattering (SANS) has provided the opportunity for the morphology of solutions of anisotropically shaped surfactant micelles to be probed in detail and for the effects of shear on such structures to be investigated. The shear dependence of the scattering from rigid monodisperse rods in dilute solution can be described quantitatively [3]. However, for systems of interest this regime is rarely encountered. Using examples from some

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ionic [sodium dodecyl sulfate (SDS) and dodecyldimethyl ammonium chloride (DDAC)] and nonionic (hexaethylene glycol monododecylether, $C_{16}E_6$, and $C_{16}E_8$) surfactant micelles, we describe some of the complications [4] due to finite-concentration effects (hindered rotation), flexibility, and shear-induced structural changes. The existence of intermicellar interactions can profoundly affect the nature of the scattering [5] and render quantitative analysis difficult. However, SANS can still provide essential insight into the structure of such micellar solutions. This is demonstrated with the shear-induced changes in the viscoelastic mixed surfactant solution of SDS and tetradecyl dimethyl ammonium propane sulfonate (TDPS) and in the mixed nonionic surfactant lamellar phase of a dioleyl cationic and 2-ethyl hexylglycerol monoether. In the latter example the ability to make scattering measurements both in the direction orthogonal (through the cell centre) to the flow and in the flow direction (through the cell side) is shown to be an important factor.

2. MEASUREMENTS

The SANS measurements were made on the LOQ diffractometer [6] at the ISIS pulsed neutron source, Rutherford-Appleton Laboratory, UK. The diffractometer uses the white beam time-of-flight method to record the scattering over the Q range 0.005 to 0.25 Å^{-1} in a single measurement.

A Couette shear-flow cell with a 0.5-mm gap and designed specifically for SANS measurements [1] was used with shear rates (G) in the range 0 to 25,000 s^{-1}. In the normal scattering geometry the neutron beam is incident normal to the axis of rotation of the Couette cell, that is, perpendicular to the flow direction and parallel to the shear gradient. Measurements have also been made through the side of the cell, in the direction orthogonal to the shear gradient.

All the micellar solutions were made in D_2O. $C_{16}E_6$ and $C_{16}E_8$ were obtained from Nikkol, Japan, SDS, TDPS, and D_2O were from BDH, and all were used without further purification. DDAC, dioleyl cationic, and 2-ethyl hexylglycerol monoether were synthesized at Unilever Research, Port Sunlight.

3. RESULTS

3.1. Shear-Induced Transformations in Dilute Systems

The effects of concentration, flexibility, and polydispersity on the shear alignment and on shear-induced structures in dilute solutions of rod-like micelles are described.

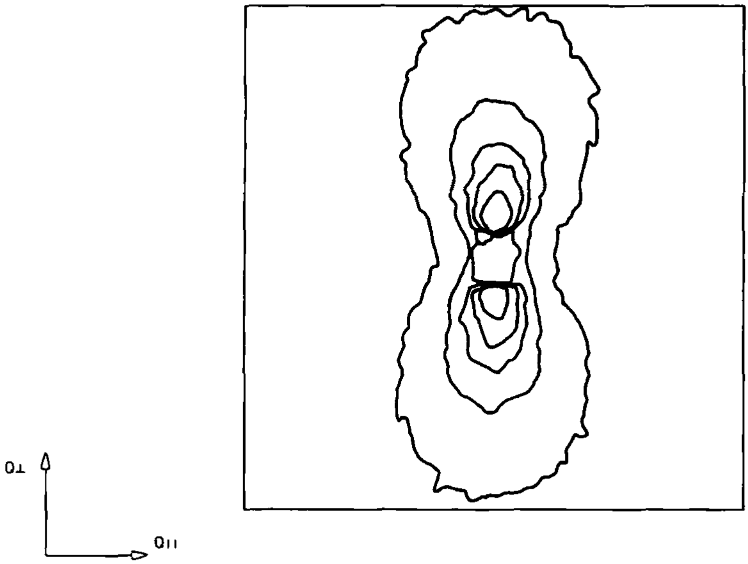

Fig. 1. Measured intensity contours for 0.04 M DDAC/4 M NaCl/D_2O at $T = 298$ K and $G = 7000\ s^{-1}$.

Analytic expressions for the shear-dependent orientational distribution of dilute solutions of rigid monodisperse rods, based on the original work of Peterlin and Stuart [7], have been derived [3]. They have been used in conjunction with the form factor for rod-like particles to form the basis of the quantitative analysis of the shear-dependent scattering from rod-like micelles [4, 8]. Most of the systems studied by us [4, 8] show a two-dimensional scattering pattern under shear, consistent with this analysis. Some systems, however, show deviations from this simple model. DDAC [8], for example, shows a scattering pattern which has more intensity in the off-symmetry directions as shown in Fig. 1. Computer simulations suggest that this is associated with flexible rather than rigid rods. Other systems investigated by us have shown similar trends [8]; and there has been much conjecture about the flexible nature of rod-like micelles [9, 10], for which the expression "worm-like" micelles has been coined.

Pronounced polydispersity can have a profound but different effect on the form of the scattering patterns under shear [8] and gives rise to increased scattering in the symmetry directions. Figure 2 shows the scattering from a 1% solution of the nonionic surfactant $C_{16}E_8$ in the mixed solvent of 80% glycerol/D_2O/0.2 M sodium thiocyanate at a shear of 5000 s^{-1} and is consistent with a broad polydisperse distribution which may well be shear-induced. The changing of solvent quality by the addition

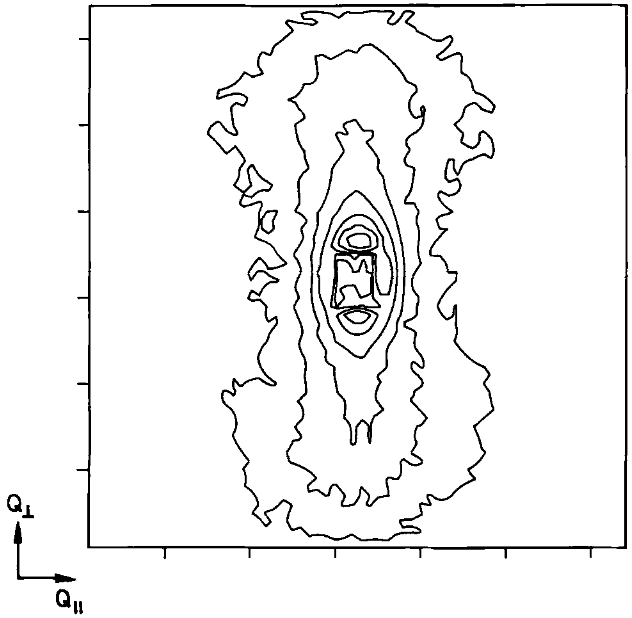

Fig. 2. Measured intensity contours for 1% $C_{16}E_6$ in 80% glycerol/D_2O/0.2 *M* sodium thiocyanate at $T = 308$ K and $G = 5000\ s^{-1}$.

of glycerol has changed the nature of the micellar distribution as the glycerol molecules specifically bind to the ethylene oxide groups of the $C_{16}E_8$. In the extreme it is difficult to distinguish between a broad polydisperse distribution of micelle sizes and the possibility of shear-induced structures. The scattering pattern presented here is consistent with the growth of a much less anisotopic micelle with increasing shear. These shear-induced structural changes have been seen in other work [11], where, for example, with increasing shear mixed micelles of C_{16}TAB and $C_{12}E_2$ transform from rod-like micelles into lamellar droplets. The application of shear in this case causes a shift in the phase boundary between the two phases.

For rigid elongated particles it is expected that the anisotropy in the scattering pattern will saturate, or reach some plateau value, with increasing shear. This predicted behavior is seen in many of the systems, such as SDS and $C_{16}E_6$, and is shown for 0.05 *M* SDS in 1.3 *M* NaCl/D_2O in Fig. 3. For deformable or flexible particles the situation is quite different. It has been shown from early light-scattering work, birefringence [12], that the shape of such a curve can then be quite different. This will also arise if there are marked shear-induced changes in the micellar structure, such as

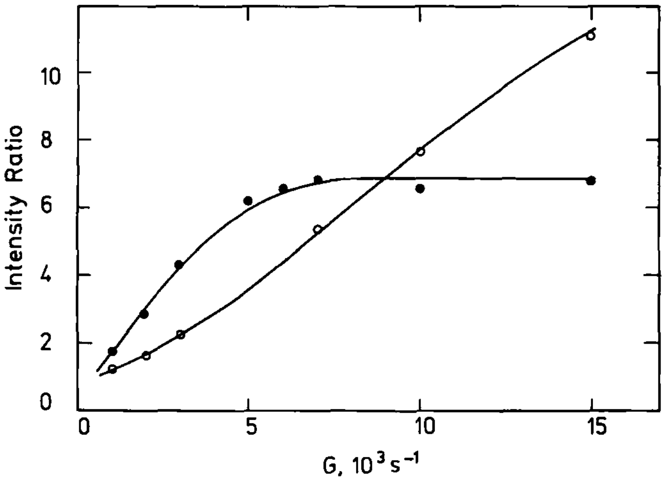

Fig. 3. Ratio of scattered intensities in direction perpendicular and parallel to flow ($Q_\perp$ and $Q_\parallel$) at a Q of 0.015 $Å^{-1}$ for (●) 0.05 M SDS/1.3 M NaCl/D_2O and (○) 1% DDAC/4 M NaCl/D_2O at $T = 298$ K.

growth, in the size distribution, or due to lifetime effects. Shown in Fig. 3 also is the shear dependence of the scattering anisotropy for 1% DDAC in 4 M NaCl/D_2O, and consistent with earlier observations the shear dependence of the anisotropy in the scattering is indicative of flexibility or deformation.

From the quantitative analysis described earlier it is possible to obtain an "effective" rod length from the shear dependence of the scattering. However, the surfactant systems studied are rarely in the dilute regime ($C > 1/L^3$, where L is the rod length). The anisotropy in the scattered intensity is then apparently larger at low shear than predicted theoretically [4]. At low shear, with a low degree of alignment or orientational order, rotational diffusion is hindered due to entanglements and collisions. This gives rise to a larger "effective" rod length at low shear, and the effects of the finite concentration are minimized only at high degrees of order. For SDS we have shown that the effects decrease with decreasing concentration [4]. However, DDAC elongated micelles, discussed earlier in the context of flexibility and shear-induced deformations, show no such hindering [4]. This has been observed more recently in some more complex mixtures. Figure 4 shows the shear dependence of the effective rod length for 1% $C_{16}E_6$ in D_2O and is typical of systems displaying hindered rotational diffusion. This contrasts with the shear dependence for the same system in the mixed solvent 35% sorbitol/D_2O. Here the supposition is that the

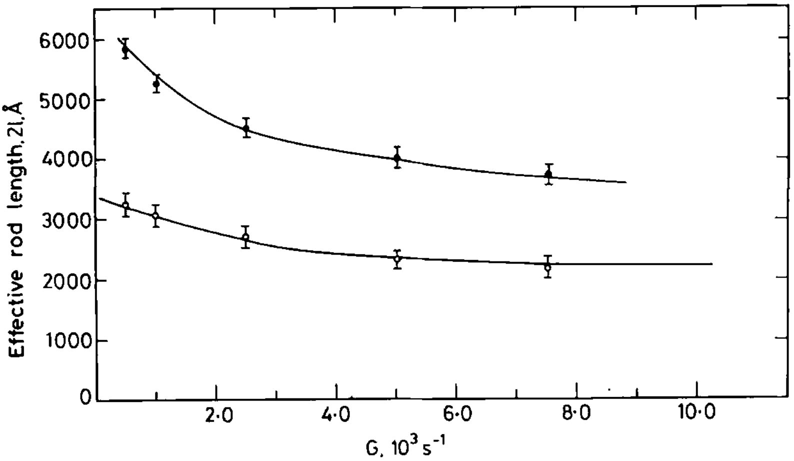

Fig. 4. Variation of "effective" rod length with shear for (●) 1% $C_{16}E_6/D_2O$ and (○) 1% $C_{16}E_6$/35% sorbitol/D_2O at $T = 303$ K.

preferential binding of the sorbitol to the ethylene oxide group reduces intraheadgroup interactions and renders the micelle more labile, resulting in a greater susceptibility to shear-induced changes.

3.2. Shear-Induced Structures in Concentrated/Interacting Systems

The existence of intermicellar interactions can profoundly affect the nature of the scattering, and a well-pronounced peak in the scattering arises. We have demonstrated that for the cationic–nonionic surfactant mixture of $C_{16}E_6/C_{16}TAB$ [5], the position in Q of the interaction peak is invariant with shear, due to the "local ordering" [13] which occurs in such strongly interacting systems. Furthermore, the position of the peak has a $C^{1/2}$ dependence as predicted theoretically [13], which is essentially a manifestation of the reduced dimensionality of the system. The surfactant mixture of SDS/TDPS, in the viscoelastic region of its phase diagram [3], has pronounced intermicellar interactions and shows marked alignment (and anisotropy in the scattering) with shear (see Fig. 5). Under shear, the scattered intensity has an interaction peak at different Q values in the directions perpendicular and parallel to the flow direction, as shown in Fig. 6, which is in contrast to the observations for the $C_{16}E_6/C_{16}TAB$ mixture. The scattered intensity under shear is now reminiscent of that observed for oriented nematic phases and is consistent with the formation of a shear-induced nematic phase as observed in a different system recently by Berret *et al.* [14].

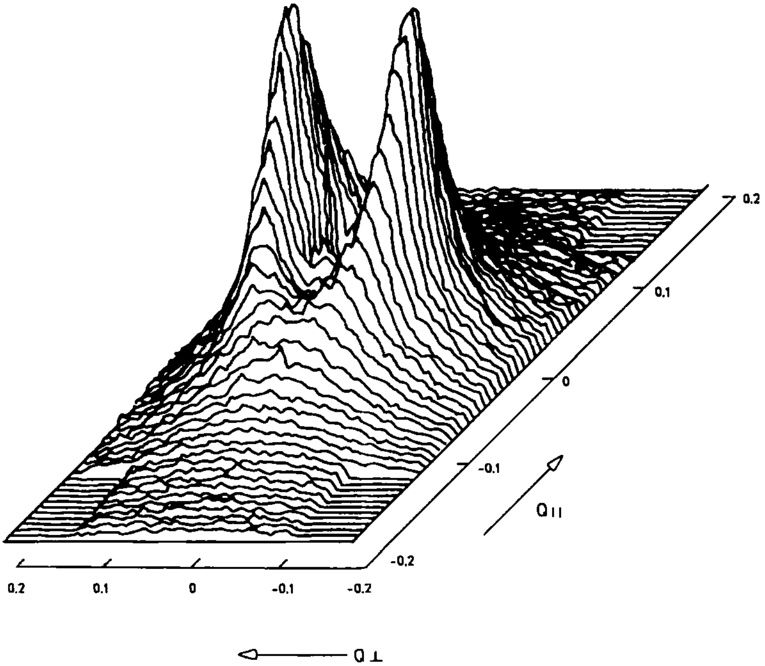

Fig. 5. Isometric plot of scattered intensity for 3.22% SDS/3.22% TDPS in D_2O at a shear gradient, G, of 1500 s^{-1} and $T = 308$ K.

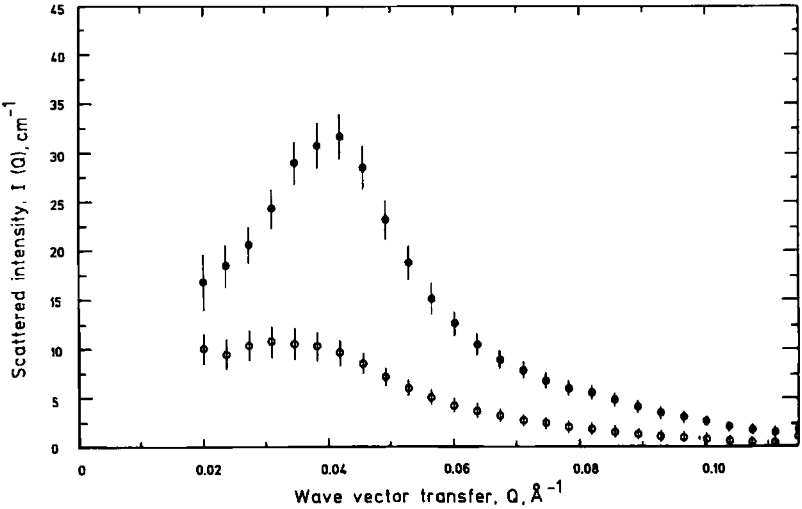

Fig. 6. Scattered intensity, $I(Q)$ (cm^{-1}), versus wave vector transfer, Q ($Å^{-1}$), for 3.22% SDS/3.22% TDPS in D_2O at a shear gradient, G, of 1500 s^{-1} for (●) Q perpendicular and (○) Q parallel to the flow direction.

There has been much recent interest in the effect of shear on lyotropic lamellar phase dispersions [15]. SANS has proved to be an important technique in the investigation of the shear-induced formation of monodisperse multilamellar vesicles from oriented lamellar phases, as reported by Diat and Roux [15] for the system SDS, pentanol, dodecane, and water. Khan Lhodi *et al.* [16] have made similar observations on the binary surfactant mixture of a dioleyl cationic and 2-ethyl hexyglycerol monoether at a surfactant concentration of 12.5% at room temperature. At zero and low shear this lamellar phase dispersion is essentially perfectly aligned with the axis (flow direction) of the Couette cell. In these circumstances there is little or no scattering when the neutron beam is incident in the direction orthogonal to the flow (through the cell center), and any residual scattering arises only from defects and any unaligned fraction of the dispersion. With the neutron beam incident in the direction parallel to the flow (through the cell side) the pronounced anisotropic scattering indicative of an highly oriented lamellar phase is observed (see Fig. 7).

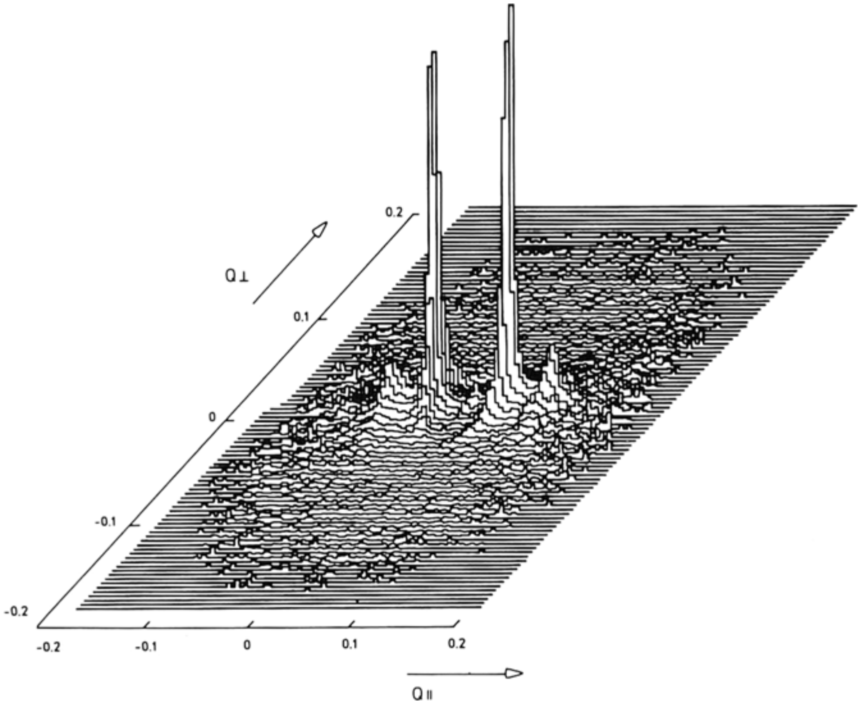

Fig. 7. Isometric plot of scattered intensity through the side of the Couette shear cell for a 12.5% dioleyl cationic surfactant and 2-ethyl hexylglycerol monoether mixture at $G = 0\ \mathrm{s}^{-1}$.

The first-order (and second) Bragg peaks observed are consistent with a d-spacing (or repeat distance) of 142 Å. With time, during the application of a shear gradient of 25 s^{-1}, the scattering becomes isotropic and more intense in the conventional scattering geometry (through the cell centre). These changes are consistent with the formation of multilamellar vesicles, as observed by Diat and Roux [15]. In addition to the evidence from neutron scattering, classical light scattering gives rise to a well-defined diffraction pattern indicating that the monodisperse multilamellar vesicles are ordered on a hexagonal lattice [16].

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