In-situ rheological x-ray scattering studies of shear induced non-equilibrium phenomena in bilayer forming phases of a mixed surfactant system.

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We have investigated using in-situ rheological small angle x-ray scattering, the structural evolution under flow induced non-equilibrium phenomena in the nematic and intermediate mesh phases of a cationic surfactant system with strong binding oppositely charged organic counterion. We show that the macroscopic flow behaviour such as shear-induced instabililities or thixotropy or viscosity bifurcation is closely related to the shear driven ordering at a mesoscopic length scale.

We have examined the structural correlation between the thixotropic (time dependent decrease in viscosity) yield stress flow behaviour in a nematic phase and the mean orientational order parameter obtained from x-ray scattering studies. By combining time resolved x-ray scattering studies with creep measurements (by imposing a steady shear stress and following the evolution of viscosity with time) we follow the evolution of the 2D diffraction patterns during viscosity bifurcation giving rise to three distinct steady state flow behaviours identified as i) jammed, ii) rejuvenated and ii) an intermediate state of unstable flows.

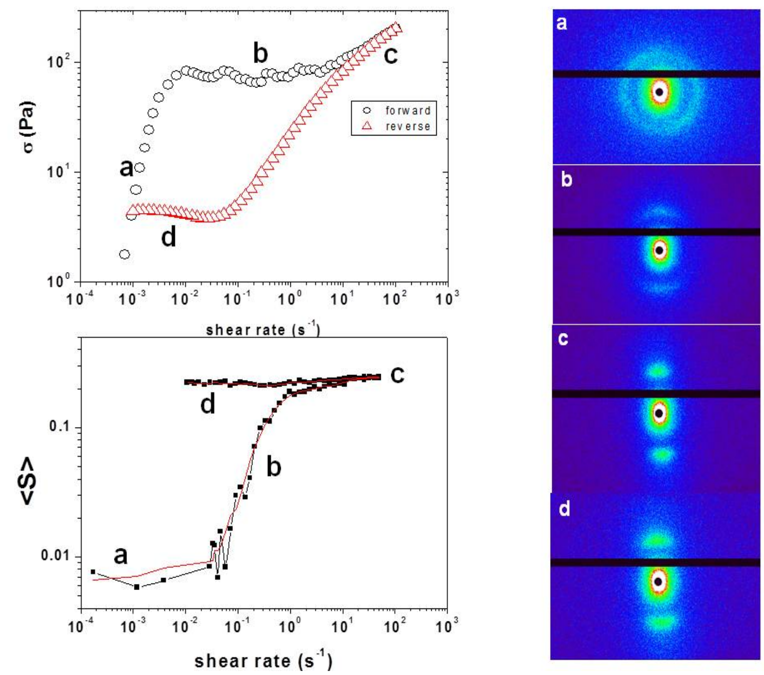

Figure 1: The evolution of the 2D diffraction pattern of the nematic gel, in a controlled shear rate flow curve (forward and reverse stress ramps) is shown. The mean orientational order parameter <S> is seen to follow the hysteresis observed in the flow curve.

Intermediate mesh phases (formed by bilayers with water filled holes or curvature defects arising from non-uniform interfacial curvature at the micelle-water interface) are known to occur between the hexagonal phase made up of cylindrical micelles and the lamellar phase made up of planar bilayers. Our studies were carried out a) in a rhombohedral mesh phase where the water filled holes are correlated across successive bilayers in an ABC arrangement and b) in a random mesh phase with no correlation of the curvature defects across the bilayers. The random mesh phase being a lamellar phase with curvature defects, we have also examined the role of these defects on the lamellar to onion transition. The flow curves obtained for the mesh phases indicate a shear thickening at intermediate shear rates (viscosity increases by a factor of 2), followed by shear-thinning behaviour. The evolution of the 2D diffraction patterns in the radial geometry at different shear rates in the Rheo-SAXS experiments, confirm that the weak shear thickening marks the onset of a lamellar to onion transition. At low shear rates an a-orientation where the bilayers align along the flow direction with the layer normal perpendicular to velocity gradient is observed as indicated by the well aligned Bragg peak. At high shear rates, the isotropic scattering pattern indicates the formation of multi-lamellar vesicles. Though the diffuse peak due to the scattering from the defects in the plane of the bilayers do not evolve under shear, the lamellar d-spacing decreases with shear rate, suggesting that the water is squeezed out of the multi-lamellar vesicles into the interstitial volume, thus accounting for the shear-thinning behaviour at higher shear rates.

Rheo-SAXS facility with the synchrotron X-ray beam passing vertically through a plate/ plate geometry has allowed the investigation of microstructural transitions under shear of highly viscous concentrated lyotropic mesophases such as intermediate mesh phases/ nematic micellar gels for the first time. Many of the macroscopic flow behaviour observed in the present study can arise from shear banding effects. In the present experimental geometry since the x-ray beam passes along the velocity gradient, it is not feasible to examine the structural rearrangements across the shear bands. Hence it is important to carry out these experiments in a couette geometry, with a vertical beam. An evaporation blocker/humidity controlled chamber with the plate/plate or cone/plate geometry will also help to prevent any artefacts in the measurements due to solvent evaporation.

Yield stress and thixotropy in a nematic micellar gel.

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