ESRF	**Experiment title:** Shear Experiments on Bilayer Phases Prepared in-situ by a Hydrolysis Reaction without Prior Shear	**Experiment number**: SC-601
Beamline: ID02A	**Date of experiment**: from: 8. 9. 99 to: 11. 9. 99	**Date of report**: 30. 8. 2000
Shifts: 8	**Local contact(s)**: Narayanan Theyencheri	*Received at ESRF:*

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Report:

The transition of a phase of planar lamellae to a phase of multilamellar vesicles has been studied by SAXS experiments in a Couette shear cell for various applied shear rates and different chemical composition of the surfactant system. In order to have a well-defined and reproducible starting state the lamellar phase was prepared directly in the Couette cell. For this purpose to an isotropic L_3-phase of composition: 100 mM tetradecyldimethylamine oxide (TDMAO)/220 mM hexanol/water 10 mM diethyl oxalate was added. The added ester does not change the original L_3-phase significantly and therefore the starting state of the system is not affected by any shear history (as the L_3-phase relaxes quickly).

However, by the hydrolysis reaction of the ester the zwitterionic TDMAO becomes charged and the L_3-phase transformed into a phase of planar lamellae. This transformation process is nicely observed in the SAXS experiment (fig. 1). One finds the originally present broad peak of the L_3-phase at short times, which becomes supplemented by a sharp lamellar peak at intermediate times, and for times longer than 40 mins only the lamellar peak remains present. This means that the formation of the lamellar phase takes place via a microscopic two-phase region L_3/L_α while macroscopically the system remains homogeneous.

After turning on the shear the scattering pattern changes significantly. A peak in the vorticity direction (135 and 315°) builds up and becomes more prominent with increasing time (fig. 2). This peak has to be due to a perpendicular orientation of the lamellae and not to the formation of vesicles since at the same time the intensity for transverse orientation of lamellae (45 and 225°) decreases for short times. For the case given in fig. 2 the relative maximum intensity for perpendicular orientation is reached after about 300 s and only afterwards the intensity for the transverse orientation (which is indicative for the formation of vesicles) starts to increase. The final state of the sample depends on the shear rate employed. In all cases multilamellar vesicles are formed but their size decreases with increasing shear rate, which is evidenced by a decrease of the pronouncedness of the lamellar peak (that almost vanishes for very high shear rates, which indicates that here almost unilamellar vesicles should be present).

Similar experiments have been done for a variety of different shear rates and for surfactants and cosurfactants of different alkyl chain length. In all cases it has been found that prior to vesicle formation always a perpendicular orientation of the lamellae is observed. Evidently for the system studied such a perpendicular orientation is a necessary prerequisite for vesicle formation. This fact that has not been observed before and opens up interesting questions regarding the detailed mechanism of vesicle formation, how the nucleation of vesicles takes place and why perpendicular orientation of the lamellae appears to be required for this process to take place.

The rate of transformation depends largely on the thickness of the bilayers, which is controlled by the alkyl chain length of surfactant and cosurfactant. The thicker the bilayer the slower are the given transformations but still they occur in a similar manner from the structural point of view. Evidently the thicker bilayers are more difficult to reoriente in the shear field but also more difficult to rupture which is necessary for the formation of vesicles.

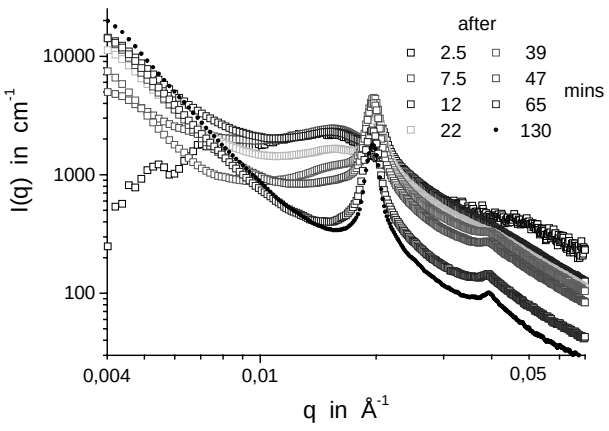

Fig. 1: *SAXS intensity for various times after starting the ester hydrolysis in the system100 mM C_{16}DMAO/ 245 mM hexanol / 10 mM diethyl oxalate*

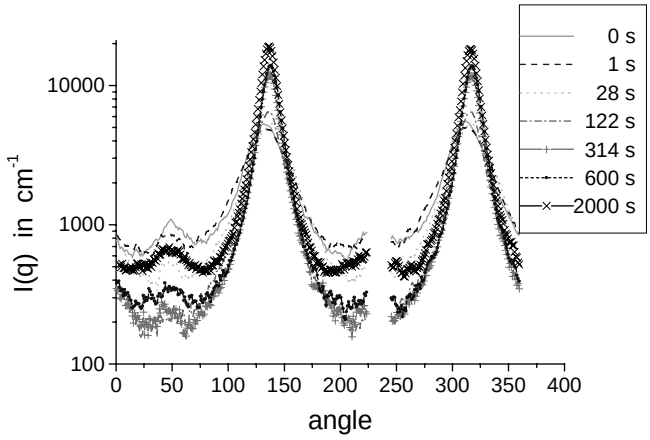

Fig. 2: *Angular distribution of SAXS intensity for various times after turning on a shear rate of 10 s^{-1} in the system 100 mM TDMAO/220 mM hexanol/10 mM diethyl oxalate*