 ESRF	Experiment title: Transient Formation of Monodisperse Unilamellar Vesicles - The Influence of the Charge Density of the Amphiphilic Bilayer	Experiment number: SC 1506
Beamline: ID02	Date of experiment: from: 19.11.2004 to: 22.11.2004	Date of report: 15. 4. 2005
Shifts: 9	Local contact(s): Thomas Weiss	<i>Received at ESRF:</i>
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Report:

Unilamellar vesicles with their single membrane and their potential for encapsulation of both hydrophilic and hydrophobic compounds are highly interesting systems with respect to applications in pharmacy, cosmetics etc. A typical system where unilamellar vesicles are formed spontaneously are mixtures of cationic and anionic surfactants [1]. In such mixtures well-defined unilamellar vesicles are formed where the time scale of formation can vary largely from the seconds range [2] to days and weeks [3, 4]. Earlier investigations showed that vesicle formation in such systems evolves via disc-like aggregates and that final size and polydispersity of the vesicles dependent largely on the structure of the intermediates [5-7]. Therefore detailed knowledge about the formation process is the prerequisite to influence the formation process via intermediately formed aggregates. It is to be expected that changes of the electrostatic conditions in the surfactant mixtures should have a large effect on their interactions and as well on the formation kinetics of initial aggregates.

In our experiments we studied mixtures of the anionic perfluoro surfactant lithium perfluorooctanate (LiPFO) and the zwitterionic hydrocarbon surfactant tetradecyldimethylamine oxide (TDMAO) with a total surfactant concentration of 100mM and with varying molar fraction of LiPFO in the surfactant mixture of 0.35-0.7. In this experiment we substituted between 0-100% of the zwitterionic TDMAO with the cationic tetradecyltrimethylammonium bromide (TTABr) thereby systematically varying the charge conditions in our systems in order to study the influence of the surface charge of the aggregates on the aggregation behaviour.

An instrument set-up with a sample-detector distance of 3m was used. To ensure reproducibility and to gain a better time resolution of the formation process the development of most mixtures was observed over a long time range with a low time resolution and the mixing process was repeated with a higher time resolution and a shorter overall measurement time. All measurements were corrected for the electronic background and electronic effects from the ccd-camera. The radial average was calculated and the background scattering from the solvent water was subtracted. All calculations were performed by standard procedures of ESRF.

While mixtures of LiPFO with TDMAO showed formation of monodisperse vesicles via disc-like micelles charging of the aggregates by replacing TDMAO with TTABr lead to a totally different formation behaviour. Initially large planar objects can be observed. Those objects reorganize into a mixture of micelles and planar objects and from this intermediate state to vesicles. This effect can already be observed and is most pronounced when only 20% percent of the TDMAO is replaced by TTABr.

The structures that are formed after about 20 min depend highly on the amount of TTABr in the solution. At very low (0%, Fig. 1) and very high (100%, Fig. 6) TTABr concentrations monodisperse vesicles of about 15 nm radius are formed. In the intermediate regions the vesicles are much larger and more polydisperse or evolve into large lamellar structures (Fig. 3).

At high TTABr concentrations (80% and 100%, Fig. 5 and Fig. 6) monodisperse vesicles can already be observed at short time ranges, as indicated by a minimum around 0.3 nm^{-1} . After some seconds micelles appear (seen in the high q -range) that are again transformed into vesicles after some minutes. For 40-60% TTABr content the scattering patterns are even more complex, starting from unstructured lamellae, then forming first unilamellar vesicles, then small micelles and finally are transformed to planar lamellae again. Apparently the formation process with the zwitterionic/cationic surfactant mixture proceeds in a much more complex way due to the different mixing affinity of the zwitterionic and the cationic.

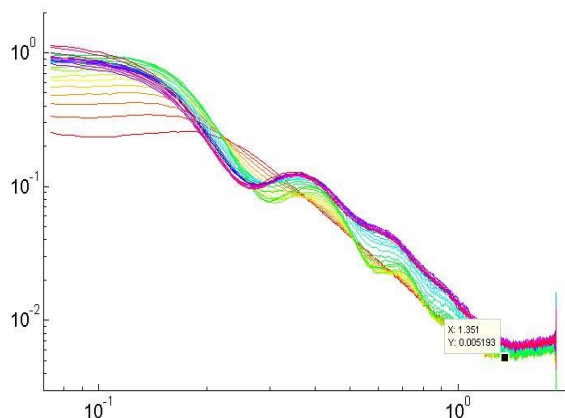


Fig. 1: Radially averaged SAXS diffraction pattern for LiPFO:TDMAO/TTABr (5:5), 0% TTABr, $c_{tot}=100m$

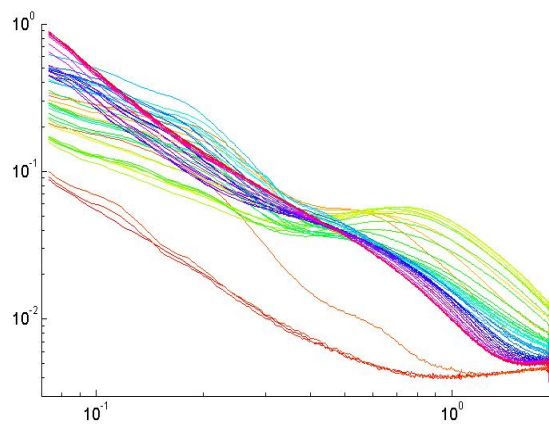


Fig. 2: Radially averaged SAXS diffraction pattern for LiPFO:TDMAO/TTABr (5:5), 20% TTABr, $c_{tot}=100m$

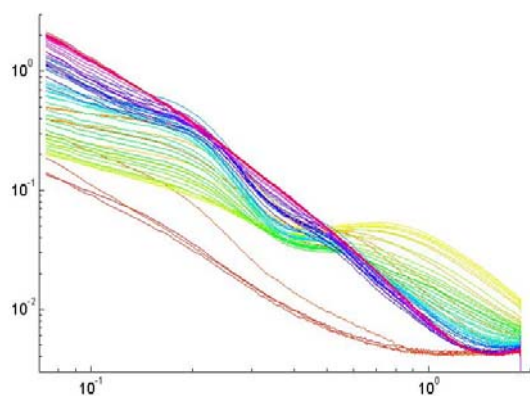


Fig. 3: Radially averaged SAXS diffraction pattern for LiPFO:TDMAO/TTABr (5:5), 40% TTABr, $c_{tot}=100m$

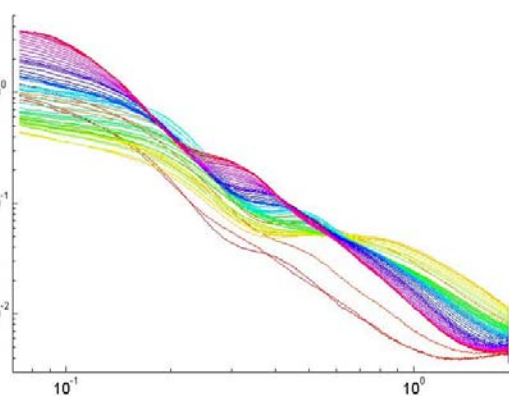


Fig. 4: Radially averaged SAXS diffraction pattern for LiPFO:TDMAO/TTABr (5:5), 60% TTABr, $c_{tot}=100m$

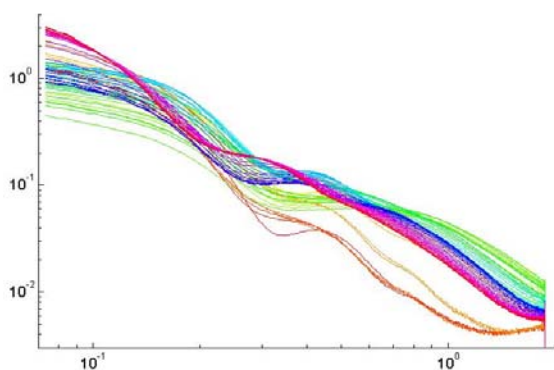


Fig. 5: Radially averaged SAXS diffraction pattern for LiPFO:TDMAO/TTABr (5:5), 80% TTABr, $c_{tot}=100m$

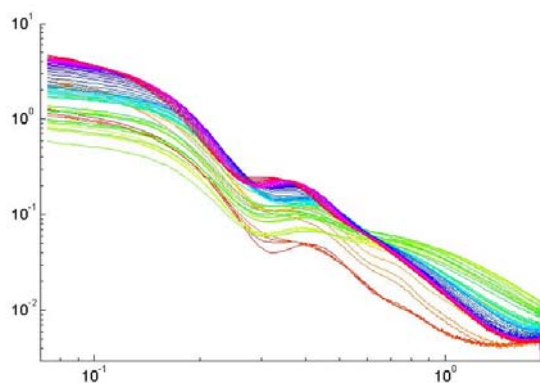


Fig. 6: Radially averaged SAXS diffraction pattern for LiPFO:TDMAO/TTABr (5:5), 100% TTABr, $c_{tot}=100m$

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