



	Experiment title: Shaping of vesicles - Control of Structure and Stability of Unilamellar Vesicles by Addition of Amphiphilic Copolymer	Experiment number: SC-3639
Beamline: ID02	Date of experiment: from: 28/06/2013 to: 01/07/2013	Date of report: March 20, 2015
Shifts: 9	Local contact(s): Dr. Theyencheri NARAYANAN	<i>Received at ESRF:</i>
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Report:

Previous investigations have shown that the formation of vesicles in zwitterionic and cationic mixtures often passes through an intermediate state of disc-like micelles before closing to form vesicles [1-4]. By addition of an amphiphilic copolymer this process can be modified and thereby one has control over the size and largely enhanced stability [5]. This result obtained on a model system shall now be extended to systems relevant for applications. Aim of the experiments carried out at ID02 was to examine in detail how this intermediate state and the possibility to control the finally formed vesicles depend on the specific interaction between the surfactant system chosen and the copolymer. This shall lead to a generalized understanding necessary in order to apply this concept to a shaping of vesicles as interesting for future applications.

For that purpose we investigated two classes of systems, where spontaneous formation of unilamellar vesicles is achieved by mixing:

- cationic hydrocarbon surfactants [6] (NaOleate + C₁₀TAB or C₁₂TAB) at $c_{tot} = 50$ mM
 - mixtures of a hydrocarbon surfactant and a cosurfactant [7] (NaOleate + 1-Octanol).
- The amount of amphiphilic copolymer of the Pluronic type (PEO-PPO-PEO, mainly L35 and F38) with respect to the mass of NaOleate was up to 10 wt% for both systems.

As experimental setup, a sample-to-detector distance of 2.5 m was chosen. To increase the time resolution of the experiment, each mixture was measured several times using different dead times after mixing. In all experiments carried out during the beamtime, a time-dependent evolution of the scattering intensity could be observed.

For the catanionic system (NaOleate + C₁₀TAB or C₁₂TAB), it was shown that a slight excess of NaOleate is favourable for the formation of monodisperse vesicles. In the case of NaOleate + Decyltrimethylammonium bromide (DeTAB) - similar to the model system TDMAO + LiPFOS - an influence of the Pluronic on the kinetics of the system could be seen. As an example, data for different Pluronic content at the same time after mixing are shown in figure 2. Although the experiments in the stopped-flow device were not perfectly reproducible (which is most likely due to problems with some remaining surfactant solution in the capillary cell between experiments), the radius of gyration shows that the more Pluronic L35 is added to the system, the bigger the final vesicle structures and the slower their growth process. This effect is subject of further ongoing more quantitative analysis of the different systems. The kinetics of formation of the unilamellar vesicles was too fast to be observed: only 25 ms after mixing, the first measurement already showed vesicular structures. However, their subsequent evolution is very well resolved by the stopped-flow SAXS experiments. An exemplary set of time-resolved data for this system is shown in figure 1.

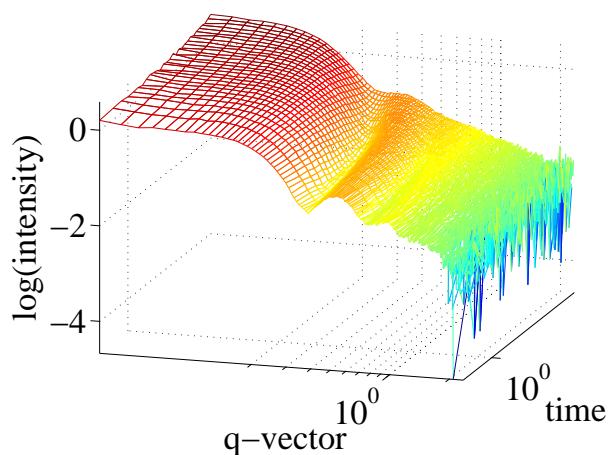


Fig. 1: Time-resolved SAXS curves of NaOleate:DeTAB = 27.5 mM:22.5 mM, 2 wt% L35, $c_{tot} = 50$ mM. (units: $[q] = \text{nm}^{-1}$, $[t] = \text{s}$, $[I] = \text{cm}^{-1}$)

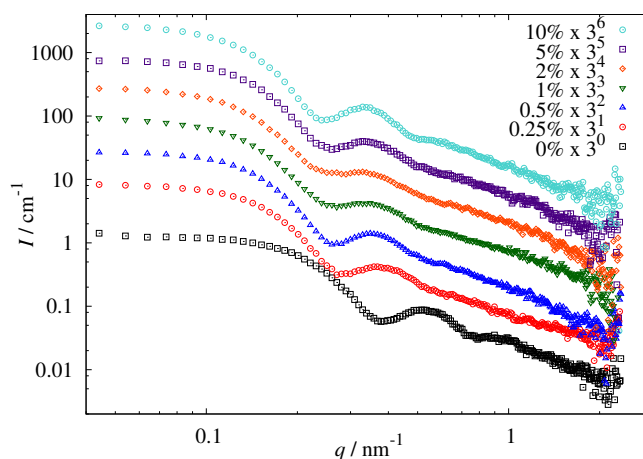


Fig. 2: Comparison of 0.25, 0.5, 1, 2, 5 and 10 wt% L35 content for NaOleate:DeTAB = 26.25 mM:23.75 mM, $t = 45$ ms after mixing

For the system NaOleate + Cosurfactant (1-Octanol), the samples investigated were viscous and clearly showed structure factor peaks dominating the scattering intensity. The analysis of the vesicle formation in these systems is ongoing and presumably proceeds via a rodlike intermediate state. A kinetic structural model for the analysis of the evolution of the scattering data is in progress.

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