

 ESRF	Experiment title: Controlling Vesicle Formation and Structure by Electrostatic and Steric Interactions	Experiment number: SC 2775
Beamline: ID02	Date of experiment: from: 2.10.2009 to: 2.10.2009	Date of report: 2.2.2010
Shifts: 9	Local contact(s): Jeremie Gummel	<i>Received at ESRF:</i>
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Report:

The mechanism of vesicle formation is still not fully understood despite the fact that it has been studied to some extent in the past [1,2]. Especially unilamellar vesicles are interesting model systems for encapsulation of hydrophilic and lipophilic compounds but as well for aggregation processes.

Earlier investigations [3-5] have shown that the formation process often passes through a disc-like intermediate that closes to small monodisperse vesicles that grow in size while the size distribution broadens. Spontaneous vesicle formation is often observed in mixtures of anionic and zwitterionic surfactants as well as in mixtures of anionic and cationic surfactants. Those systems are therefore adequate to study spontaneous vesicle formation and the influence of the charge of the aggregates on the stability of the products or intermediates by exchanging the zwitterionic surfactant by a cationic surfactant.

Since the transition between the disc-like aggregates and the vesicles is mostly controlled by the balance between the line tension of the disc-rim and the bending energy of the vesicle membrane another possibility to influence the stability of those transitional aggregates is to add a hydrophobically modified water soluble polymer. These polymers might most likely accumulate at the disc-rim and therefore decrease the line tension, which should lead to larger disc-like micelles and therefore larger vesicles. The general aim of these modifications by ionic surfactant of amphiphilic copolymer is to the formation process and the structure of the formed vesicles by the molecular composition of the vesicle forming amphiphilic system.

In our experiment we studied mixtures of the anionic perfluoro surfactant lithium perfluorooctanesulfonate (LiPFOS) and the zwitterionic hydrocarbon surfactant tetradecyldimethylamine oxide (TDMAO) with a total surfactant concentration of 50mM and with varying molar fraction of LiPFOS in the surfactant mixture between 0.3 and 0.7. In the first part of the experiment we substituted between 0-40% of the zwitterionic TDMAO with the cationic tetradecyltrimethylammonium bromide (TTABr) to study the influence of the surface charge of the aggregates on the aggregation behaviour.

In the second part of the experiment we studied the influence of polymers on the line tension of the disc-like micelles and on the steric interactions of the aggregates by adding a hydrophobically modified polymer to the mixture so that the polymer concentration was between 1 to 10% of the TDMAO concentration. We used two polymers of the Pluronic type, the Pluronic L35 (EO₁₁PO₁₆EO₁₁) and F38 (EO₄₆PO₁₆EO₄₆), and Brij 700 (C₁₈H₃₇EO₁₀₀) to vary the length and the characteristics of the hydrophobic part of the polymer.

All mixtures were prepared in a stopped-flow device in that way that premixed TDMAO/TTABr solutions or premixed TDMAO/polymer solution with a total surfactant concentration of 50mM were added to a 50mM LiPFOS solution.

Two instrument set-ups were used with a sample detector distance of 2m and 4m to cover a large q-range. To ensure the reproducibility of the experiment and to achieve good time-resolution of the process the scattering

of every mixture was monitored over a a time range of 20 minutes with low time resolution and the mixing monitored again over a shorter time range of a few seconds with a higher time resolution.

All scattering patterns were corrected for the electronic background and the electronic effects of the ccd-detector in a standard procedure at the ESRF. The radial average of the two dimensional images was calculated using the program BerSANS and the background scattering from the solvent water was subtracted with a Matlab-application.

The experiments performed on ID02 at the ESRF were very successful. They show that substitution of TDMAO with TTABr as well as addition of polymers have a large effect on the kinetics of the process, the structure of the intermediates, and as a result as well on the vesicles formed from the disc-like micelles.

A remarkable effect was that the addition of the polymers slowed down the vesicle formation process significantly from several second without polymer to several minutes with small polymer contents. Furthermore the final size of the disc-like micelles was with about 40nm much larger than in the mixtures without polymer with a final size of about 20nm. As a consequence the initial vesicles are as well much larger in the system with polymer than in the system without polymer. The polydispersity of the initial vesicle size was very low in the system with Pluronic L35 and F38 but in the system with Brij 700 even larger as in the system without polymer.

The charge of the aggregates showed as well an effect on the initial size of the vesicles. Substitution of TDMAO with TTABr lead to slightly smaller vesicles with a narrow size distribution. These experiments show that the size and polydispersity of the vesicles as well as the characteristic time of the formation process can be influenced and tuned by addition of polymers or by surface charge variation. This means that the process of vesicle formation can be tuned and controlled to a large extent already by the admixture of rather small amounts (< 5 wt%) of amphiphilic additive. This renders such vesicle systems very interesting for potential applications where precise control of structure and kinetics of formation are required for novel use of vesicle systems. Such experiments are the main focus of our future research activities.

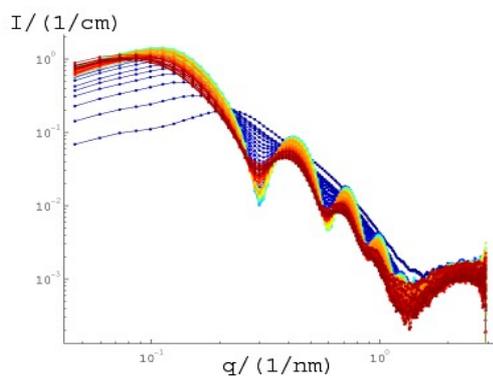


Fig. 1: Radial averaged SAXS diffraction pattern for TDMAO:LiPFOS (5.5:4.5), $ctot=50m$

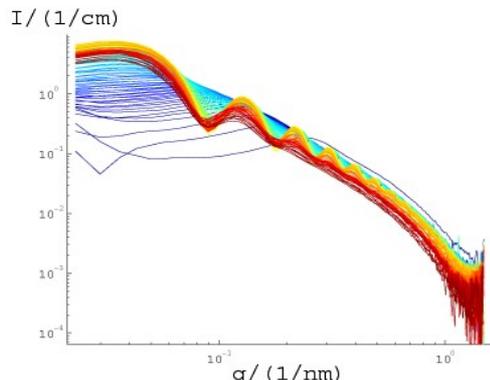


Fig. 2: Radial averaged SAXS diffraction pattern for TDMAO:LiPFOS (5.5:4.5), $ctot=50mM$, $c(Plu.L35)=0.275mM$

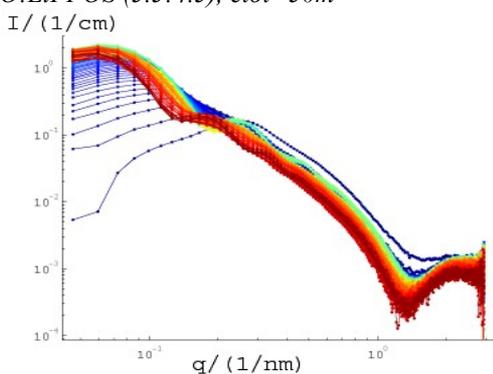


Fig. 3: Radial averaged SAXS diffraction pattern for TDMAO:LiPFOS (5.5:4.5), $ctot=50mM$, $c(Brij700)=0.275mM$

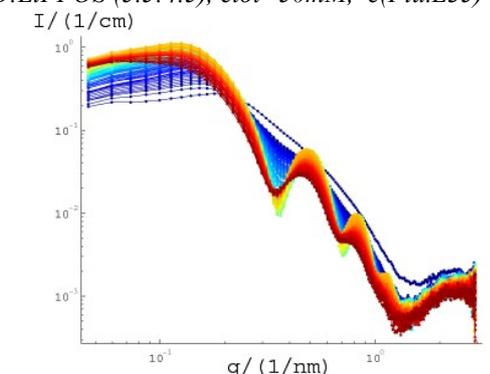


Fig. 4: Radial averaged SAXS diffraction pattern for TDMAO:TTABr:LiPFOS (4.95:0.55:4.5), $ctot=50mM$

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