Time-resolved SAXS to Elucidate Structural Changes in Amphiphilic Systems as a Basis for Controlling Self-Assembly

<u>Michael Gradzielski</u>¹*, Katharina Bressel¹, Michael Muthig¹, Jeremie Gummel² and Theyencheri Narayanan²

 ¹ – Institut für Chemie, Stranski-Laboratorium for Theoretical and Physical Chemistry, Technische Universität Berlin, Germany
² – European Synchrotron Radiation Facility (ESRF), Grenoble, France
* - michael.gradzielski@tu-berlin.de

Unilamellar vesicles are self-assembled systems that are interesting for encapsulation or as delivery systems. They can be formed spontaneously in surfactant mixtures of upon mixing surfactants and cosurfactants. However, often it is difficult to control their size and structure and in general they are prone to ageing, i.e., the structure is not well-defined over time as they are often metastable [1]. In our experiments the fast formation process in surfactant mixtures was studied by coupling the stopped-flow technique to high-flux SAXS experiments, allowing to obtain detailed structural information with a time-resolution of 5-50 ms. This was done on a model system composed of perfluorinated anionic and zwitterionic hydrocarbon surfactant, showing that it proceeds via a disklike intermediate state, yielding very monodisperse unilamellar vesicles, due to the kinetic control of this process. The size of the vesicles formed is determined by the ratio of bending constants and the line tension of the system [2]. However, these vesicles age rather quickly afterwards, thereby yielding bigger and less well-defined vesicles. Based on the detailed knowledge of the formation process it was possible to manipulate it by admixing amphiphilic copolymers. This reduces the line tension and leads to larger and very monodisperse vesicles, which now in addition are long-time stable. Accordingly by this shaping approach one obtains unilamellar vesicles with tunable radii in the range of 20-70 nm and with polydispersity indices of 0.04-0.06, which are attractive for a number of applications [3]. This means that from knowing the formation pathway this process can be controlled in a systematic fashion by the presence of copolymers and one can produce long-time stable vesicles of high structural definition.



Fig. 1 Structural progression occurring in the solutions as a function of time.

Literature:

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