



Experiment title: *Fast Micellar Kinetics: Sphere-rod kinetics of polymeric micelles and self-assembly kinetics of micelles formed by alkane-polyethyleneoxide or its oligomeric analogues.*

Experiment number:
SC2649

Beamline:	Date of experiment: from: 03.07.09 to: 03.07.09	Date of report: 22.02.10
Shifts:	Local contact(s): Dr. J. Gummel/Dr. T. Narayanan	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Reidar Lund DIPC, San Sebastian, Spain *

Grethe Vestergaard Jensen, University of Aarhus, Denmark.

Lutz Willner, Forschungszentrum Jülich, Germany*

Jan Skov Pedersen, University of Aarhus, Denmark.*

Juan Colmenero DIPC, San Sebastian, Spain

Dieter Richter, Forschungszentrum Jülich, Germany

Report:

Self-assembly of amphiphilic molecules is an extremely important process in nature responsible for a wide range of structures including the living cell itself. Here scattering techniques play a vital role – especially synchrotron SAXS combined with a stopped-flow set-up which due to the high brilliance of the beam and the rapid mixing can directly access the structural evolution in the milli-second range and hence the kinetics.

The aim of this proposal was twofold. First the intention was to investigate the formation (micellization) kinetics of low-molecular weight surfactant micelles. The idea was to compare the results to the data previously obtained from block copolymer micelles [1]. In the second part we aimed to study the early stage of a cylinder-sphere transition occurring in a system of amphiphilic block copolymer micelles.

In the preparation for the ESRF experiment, several surfactant solvent systems were investigated as candidates to study the micellization kinetics. The best contrast conditions were found for C12G2 sugar surfactants in water/dimethylformamide (DMF) mixtures where the head groups (sugar rings) show a strong positive contrast to DMF/water solutions while that of the C12 tail is negative. In addition, micellization could be easily triggered by adding water into surfactant/DMF solutions at concentrations above 7.5 mg/mL. At ID02 we performed systematic experiments of the micellization process of these surfactants using a stopped-flow apparatus. Some representative data, at 10 mg/mL 1:1 DMF/water solution, are given in Figure 1 where the scattered intensity vs. Q is plotted as a function time.

As seen in the Figure 1 a), we can observe the complete transition from unimers at short times to a gradual emergence of micelles at longer times. Thus, for the first time the complete micellization process of surfactant micelles has been observed thanks to the high flux offered in synchrotron SAXS. In order to model the scattering, we considered a general coexistence approach consisting of a linear combination of surfactant (modelled as a linear inhomogeneous “pearl necklace”) and an ellipsoidal core-shell model. As seen in Fig 1 b), the model works rather well giving the fraction of micelles and the mean radius of micelles as depicted

in c) and d) respectively. In the near future we plan to compare the structural results to a detailed kinetic model.

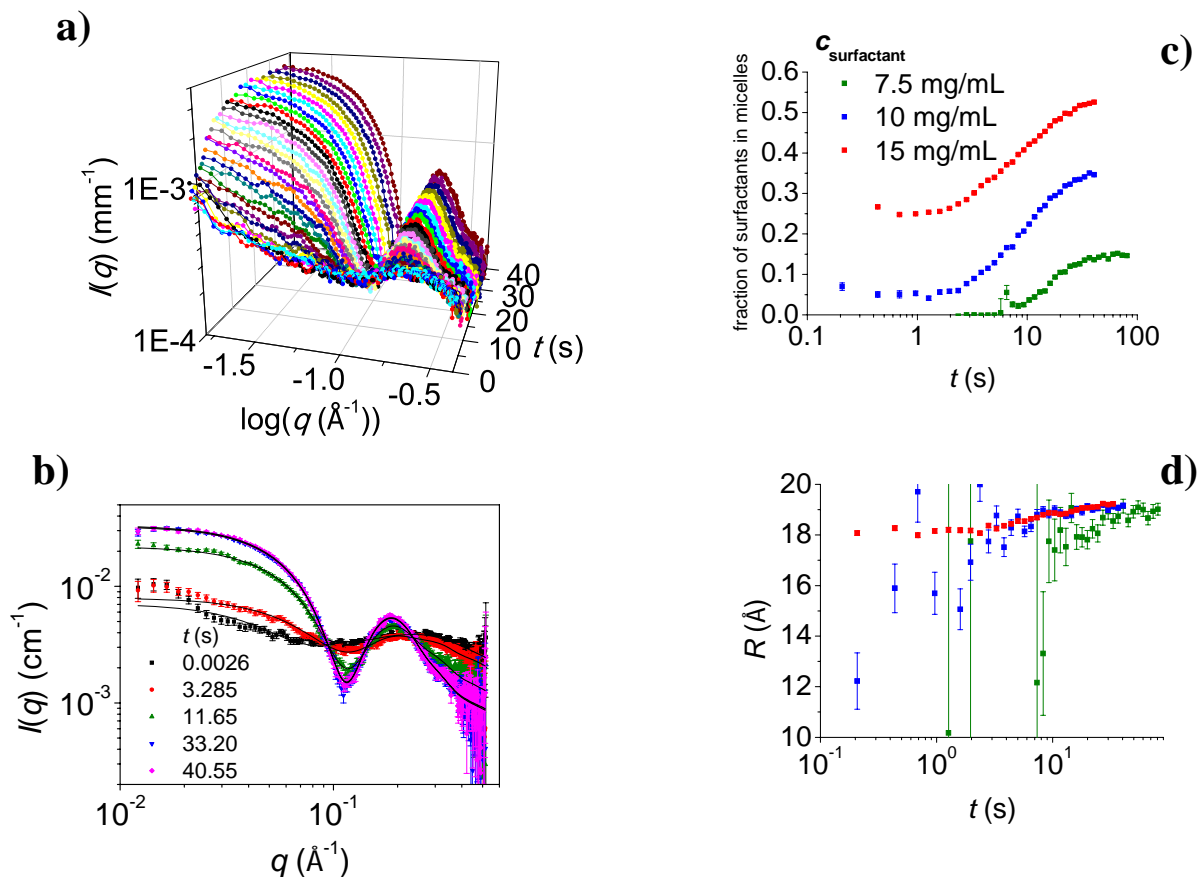


Figure 1: Micellization kinetics of C12G2 beta-dodecyl maltoside surfactants. a) shows the time resolved scattering data obtained at ID02. b) representative fits consisting of a coexistence model between ellipsoidal micelles and linear surfactants. c) extracted normalized fraction of micelles as a function of time d) time dependent micellar core radii

In the other part of the experiment we focussed on the transition from cylindrical to spherical micelles in amphiphilic poly(ethylene-alt-propylene)-b-poly(ethylene oxide) (PEP-PEO) micelles induced by addition of DMF to a water rich solution. The results shown in Figure 2 a) are rather difficult to interpret due to the near contrast match between the overall micelle and solvent for SAXS which impede a complete resolution of the morphology. Nevertheless, the experiment was also repeated with SANS (see Fig. 2 b) and progress is being made to systematically compare the data. In particular by the complimentary contrast for x-rays and neutrons, we may obtain detailed information concerning the internal micellar structure during the course of the kinetic process using SAXS, while SANS detects the overall morphology.

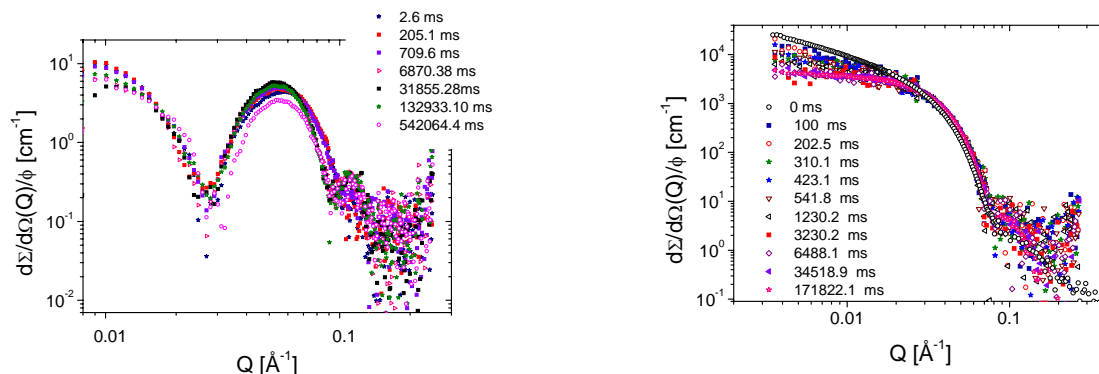


Figure 2: The cylinder to sphere transition of PEP1-PEO1 micelles in DMF/water solutions. a) shows the kinetic data obtained using x-rays at ID02 while b), represents data measured using neutrons at D11, ILL.