Experimental report

05/02/2021

Proposal:	**9-10-1597**	**Council:**	4/2019

Title: Time-resolved observation of the formation of amphiphilic surfactantsmicelles using neutron rheo-reflectometry

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Pluronic P123 / HO(CH2CH2O)20(CH2CH(CH3)O)70(CH2CH2O)20H

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	04/02/2020	07/02/2020

Abstract:

For the proposed experiment the tri-block copolymer Pluronic P123 (EO19– PO69–EO19) is used consisting of propylene oxide (PO) and ethylene oxide (EO). Being an amphiphile, P123 forms core-shell micelles (core=PPO, shell=PEO) in polar solvents depending on the temperature and concentration. At intermediate temperatures (20-40°C) the micelles can be described as spheres (diameter=17-18nm). For higher temperatures, their form changes towards cylindrical or even wormlike structures. Ordered micellar systems can be obtained for small concentrations, when the micelles are confined to an interface. The proposed experiment aims to study the time-dependent micellization of P123 at different temperatures and surface confinements. Since the ordered micellar system can be manipulated using shear, we want to go even further and destroy the micelles to look at their subsequent rebuilding process. Therefore shear rates of 1000 to 10000 1/s should be applied for a short time followed by kinetic NR measurements after shear cessation to monitor the re-equilibration process.

Experimental task and set-up:

The aim of the experiment at the FIGARO reflectometer was to study the time-resolved re-micellization of Pluronic P123's micelles after they were initially destroyed using shear. For the experiments, an Anton Paar rheometer was mounted in the sample chamber and modified to hold custom-made silicon blocks (height: 7 cm x width: 7 cm x height: 1 cm) with polished surfaces. The very high shear rates, which are necessary for destroying the micelles, were achieved using the plate-plate geometry of the rheometer and, in order to avoid an uneven sample film inside the measurement cavity (60µm), the sample environment was 'overfilled' with the Pluronic solutions. Both octadecyltrichlorsilane (OTS) coated (hydrophobic, γ~12 mN/m) and activated surfaces (hydrophilic, γ~71 mN/m) were used. Initially, the experimental plan was to heat the solutions to two temperatures, which are either in the spherical or worm-like micelles regime, afterwards induce the high shear rates and subsequently measure the reformation of the micelles during the relaxation time. In the end both static and dynamic measurements were performed at 10°C, 38°C and 70°C during a heating and cooling cycle of the sample. Each cycle started with a static measurement at 10°C during the waiting time for the solution to reach equilibrium. During the following heating ramp data was continuously acquired until reaching the next target temperature. At both 38 and 70°C the samples was sheared for several minutes and the solutions were subsequently left to relax for 20 minutes. During the following heating or cooling ramp, data was continuously acquired again. For the experiment two angular set-ups (#1: 1.4°, #2: 2.5°, $\Delta\lambda/\lambda$=7%) were used. The first angle was used during the static measurements at 10°C and during the application of shear. The second one was used during the dynamic measurements, in which the solution was either relaxing or heated/cooled. In this case an illumination time of 60s was chosen. Using the COSMOS macro in LAMP it was later possible to merge the data from both angles resulting in a large effective q-range from 0.005 up to 0.25 Å^{-1}.

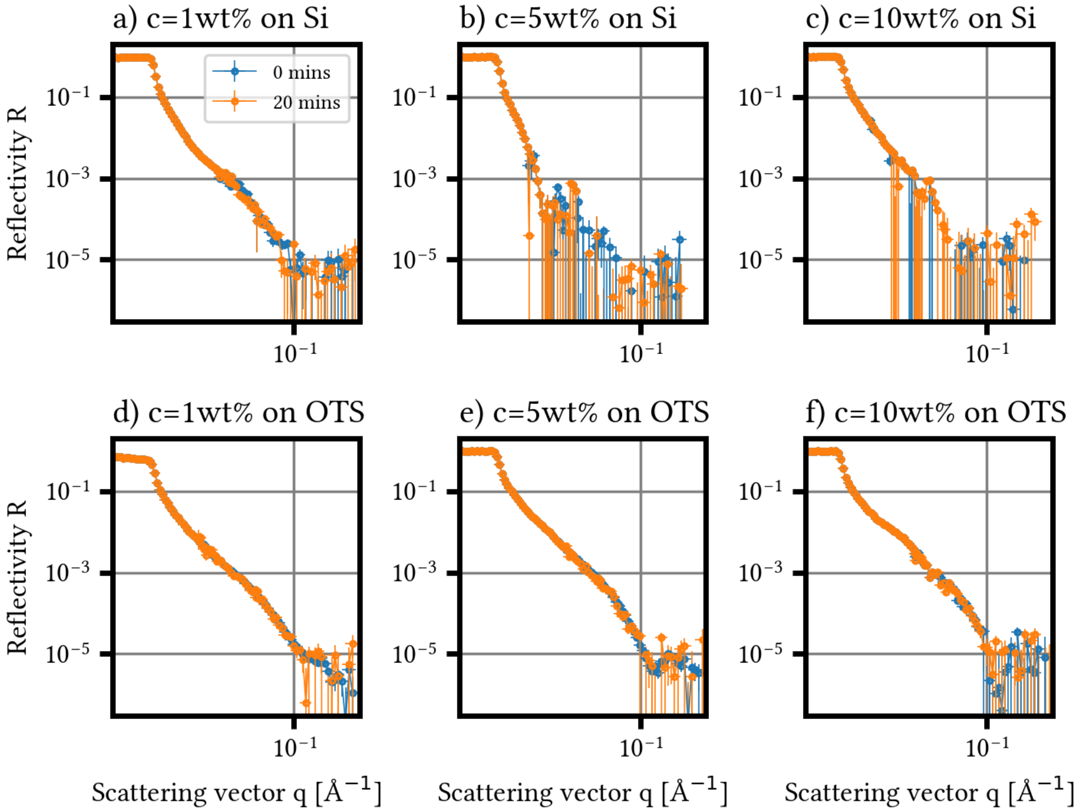

Figure 1: Reflectometry data of all measured samples on the activated or OTS-coated in the spherical micelle regime at 38°C directly after the shear has stopped (blue dots) and 20 mins after that (orange dots). The full q-range is merged from the data of both angular set-ups.

Preliminary results:

Due to prior SAXS and SANS beamtimes, the samples were changed compared to the proposal to aqueous solutions with P123 concentrations of 1, 5 and 10 weight percent (wt%). The shear rates for the experiments were produced using continuous rotations and set at 4000 s^{-1} and 20000 s^{-1} for the hydrophobic and hydrophilic surfaces, respectively. Since the shear rates depend on gap size of the rheometer, the thermal expansion of the steel rotator was measured before the experiments, so it could be adjusted before shear was applied. Despite these preliminary measurements, it was not possible to see an effect of the applied very high shear rates on the sample system, neither on the hydrophilic nor on the hydrophobic surface (see figure 1). There are two possible explanations for this apparent ineffectiveness and unresponsiveness of the system. Although the gap size of the rheometer was adjusted manually during the experiments, there were runs in which these changes were simply not applied. In the worst case (at 70°C) this would result in significantly lower shear rates than desired. However, another explanation could be the passivation of the surfaces due to a very stable layer of polymers on it, which is clearly visible in the case of hydrophobic surfaces (see figure 2, b). Test measurements with shear rates of 10^6 s^{-1} showed promising behavior. The authors are optimistic that higher shear rates, a refined experimental set-up as well as a combined analysis of specular reflectivity and the visible small-angle scattering signal could provide the desired information about the formation of P123's micelles after their shear-induced dissolution.

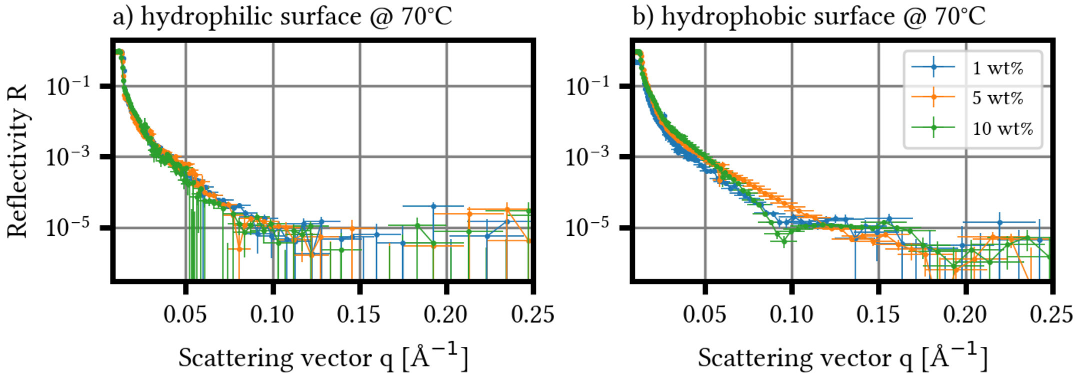

Figure 2: Experimental data at 70°C for the a) hydrophilic and b) hydrophobic surface. The shown curves are merged from the measurements at both angles and recorded during the relaxation after the shearing stopped at this temperature. All 60 s data frames of the second angle were added in case of the hydrophobic surface, while only the last data set before the start of the cooling ramp is shown for the hydrophilic surface. This is due to slight deviations in the individual curves at around 0.04 Å^{-1}.

However, the temperature-dependent reflectivity data gives useful insight in the aggregation behavior of P123 under confinement (see figure 2). During the heating of the solutions with Pluronic concentrations of 1 and 5 wt% on the hydrophilic surface, a Bragg-like peak appears at 0.04-0.05 Å^{-1} in the specular reflectivity (see figure 2, a), which is most likely due to an ordered staking of the micelles [1]. The corresponding stacking distance would be 15 nm, which is in fair agreement with the thickness of the worm-like micelles at this temperature. Interestingly, this peak does not appear during the same measurements using the OTS-coated hydrophobic surfaces (see figure 2, b). Here, a distinct oscillation between 0.09 and 0.19 Å^{-1} is visible, which indicates the presence of a passivating polymer layer near the surface of roughly 6 nm thickness. This layer is not present in the data for 5 wt% of Pluronic and the reason for that is still unknown.

The experimental data, using both the hydrophilic and hydrophobic surface, is in very good agreement with observations in bulk solutions, which are reported in literature [2]. Near the cloud point (T_{cloud} ~ 90°C for P123), the micelles undergo a third form-phase transition towards lamellar aggregates. This is probably due to a surpassing of the upper critical solution temperature of the PEO chains in the triblock polymer, which causes a phase-separation-like behavior. Our own synchrotron SAXS and SANS measurements in the temperature regime near the cloud point, could verify that the observed large aggregates have a lamellar ordering with a periodicity of roughly 6.2 nm. This would be equivalent to almost completely stretched and dehydrated polymer chains, which is expected for phase separated polymer solutions. In a preliminary analysis attempt using the model-dependent Parratt formalism, the polymer layer thickness on the hydrophobic surfaces matched the periodicity of the lamellar micelles near the cloud point (see figure 3). This is an additional indication of the necessary hydrophobic and water-free environment for the formation process of lamellar system, but a final link between behavior of bulk Pluronic solutions and under confinement is still under investigation.

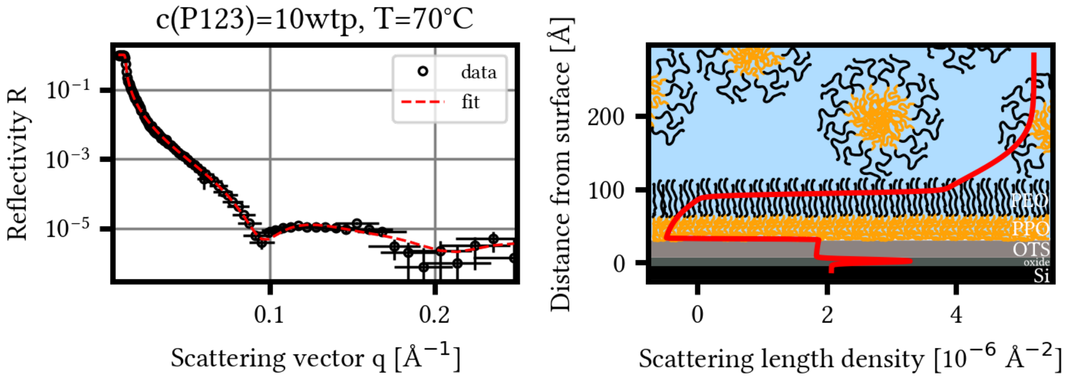

Figure 3: Fit to the experimental data of P123 solution with a concentration of 10 wt% on the hydrophobic surface at 70°C using the Parratt formalism. The resulting SLD profile exhibits a polymer layer of 6.2 nm thickness on top of the OTS coating. During modeling, the SLD of the silicon wafer ($2.07 \cdot 10^{-6}$ Å^{-1}) as well as the oxide layer ($3.47 \cdot 10^{-6}$ Å^{-1}) were fixed and the parameters of the OTS layer were precalculated [3].

Future use of the data:

The experimental data is already an integral part of one of the authors PhD-thesis (B. Sochor). Furthermore, it will be presented in an upcoming publication investigating the high-temperature structure of P123's micelles as well as the observed gelation of Pluronic solutions near their cloud point.

References:

[1] S. Gerth et al., *Journal of Physics: Conference Series* **340**, 012088 (2012)
[2] B. Hammouda, *European Polymer Journal* **46** (12), 2275-2281 (2010)
[3] M. Lessel et al., *Surface and Interface Analysis* **47** (5), 557-564 (2015)