ESRF	**Experiment title:** Dynamics of a photo-rheological micelle system by XSVS	**Experiment number**: SC4553
Beamline: ID10	**Date of experiment**: from: 28/06/2017 to: 04/07/2017	**Date of report**: 31/08/2017
Shifts: 18	**Local contact(s)**: F. Zontone, Y. Chushkin	*Received at ESRF:*

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Summary:

We studied the change of viscoelastic properties in photo-rheological fluids by X-ray Speckle Visibility Spectroscopy (XSVS) as well as X-ray Photon Correlation Spectroscopy (XPCS). Photo-rheological fluids alter their rheological properties upon light irradiation through a change in molecular structure. For instance it is possible to increase or decrease the shear viscosity. We studied a mixture of cetyl trimethylammonium bromide (CTAB) and trans-ortho-methoxycinnamic acid (OMCA) which forms wormlike micelles [1] and shows a strong response to UV irradiation (< 400 nm) [2]. Changing the isomerization from trans-OMCA to cis-OMCA by UV illumination weakens the interaction with CTAB since the cis-isomer of OMCA is less favorable for binding to the micellar interface. Additionally, cis-OMCA is less hydrophobic which further lowers the connectivity. In highly viscous samples the analysis reveals correlation functions with decay in two distinct steps: an initial decay in the millisecond regime and a terminal ergodicity restoring relaxation in the second regime.

Set-up:

The photo-induced change of viscoelastic properties was probed by XSVS and XPCS in SAXS geometry. Samples of different OMCA-CTAB ratios were prepared and filled in quartz capillaries. Here, the concentration of the ingredients and the thickness of the capillaries were chosen in order to ensure a homogeneous excitation of the whole sample volume. In order to increase the scattering signal, aluminum-doped silica particles (<50 nm diameter) were added.

As optical excitation source, a Hg-based UV lamp from Lot QuantumDesign with a power of about 100 W was used. The spectral range of the lamp covers the two absorption bands of the sample at 270 nm and 312 nm, which both can contribute to the photo-isomerization. The diameter of the light cone was as big as the length of the capillaries in order to transform the entire sample.

The experiment was performed using the standard SAXS chamber of the beamline ID10 without any special requirement on the temperature stability. Partially coherent and monochromatic X-rays with a photon energy of 21 keV were focused down to 10x10 μm^2 on the samples. The SAXS signal was collected by a Maxipix detector (CdTe version). Use of 21 keV is a game changer for this experiment which is not possible at 8 keV due to strong beam induced damage of the sample.

Results:

XPCS analysis of an un-irradiated CTAB-OMCA sample shows dynamics with time constants in the range of seconds (see fig. 1 left). The correlation curves were fitted with the Kohlrausch-Williams-Watts exponential form:

$$g^{(2)}(\tau)=\beta\cdot\exp(-2(\tau\cdot\Gamma)^{\gamma})+a$$

The decay rates ($\Gamma = 1/\tau$) show a clear q-dependence ($\Gamma \propto q^{1.3}$, see Fig. 1 right).

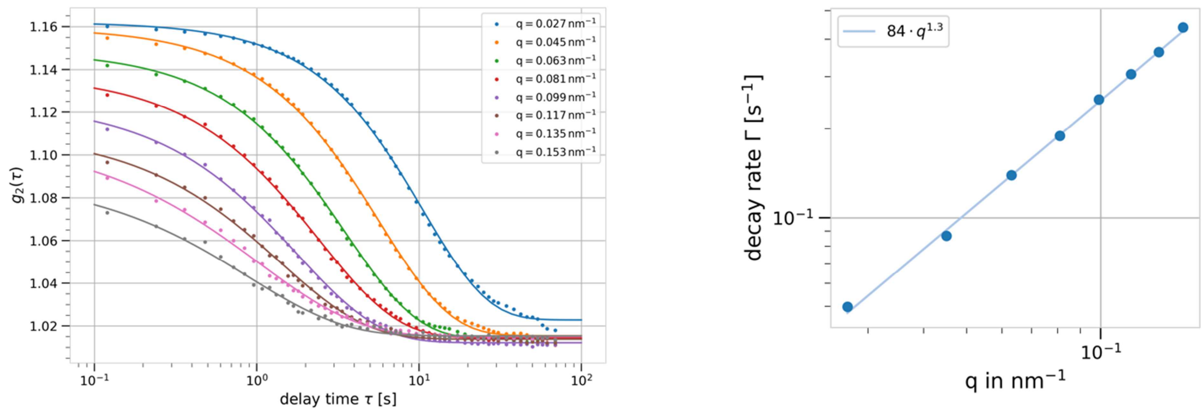

Figure 1: XPCS results of CTAB-OMCA (un-irradiated). The curves reveal dynamics in the system on the second time scale. The fitted decay rates scale like $q^{1.3}$. In addition to the decay of the correlation function a strong variance of the contrast vs q can be observed, indicating the presence of faster processes.

The XSVS measurements enable access to faster time scales. This technique relies on recording speckle image series with different exposure times. By using a speckle statistics analysis, based on the Poisson-Gamma-Distribution, the speckle contrast as a function of exposure time can be deduced (see Fig. 2). By this means, the time resolution is only limited by the minimum exposure time that can be achieved and not by the detector repetition rate like in regular XPCS. Analysis of the XSVS data revealed a second decay with time constants in the lower millisecond range (Fig. 2, right) in accordance with the change in contrast vs q of the XPCS data (Fig 1, left).

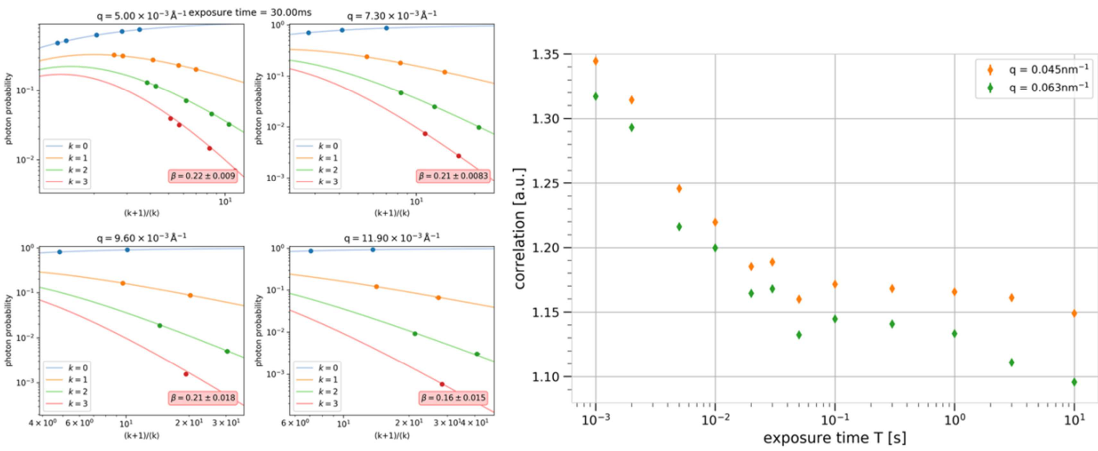

Figure 2: (Left) Photon probability distribution of a speckle image series acquired with 30 ms exposure time. The four plots show different q regions of the detector where the probability of detecting k photons in a pixel was calculated. <k> is the average photons/pixel number in the four different regions. Solid lines show fits with the Poisson-Gamma-Distribution yielding the speckle contrast β. (Right) XSVS results at two momentum transfers vs exposure time.

A systematic analysis of the data, especially regarding the influence of the UV radiation, is ongoing.

References:

[1] M. E. Cates and S. J. Candau, J. Phys.: Condens. Matter **2**, 6869 (1990)

[2]A. M. Ketner *et al*., J. Am. Chem. Soc. **129**, 1553 (2006)