



<b>Experiment title:</b> The hydration layer of the model colloid CTAB studied by non-resonant x-ray Raman scattering		<b>Experiment number:</b> HE- 3592
<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 23.07.2011 to: 27.07.2011	<b>Date of report:</b> 24.03.2012
<b>Shifts:</b> 12	<b>Local contact(s):</b> Marco Moretti Sala	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

**M.A. Schroer<sup>\*, a)</sup>, Ch.J. Sahle<sup>\*, a)</sup>, C. Sternemann<sup>\*, a)</sup>, P. Degen<sup>\*, b)</sup>, J. Smiatek<sup>c)</sup>**

a) Fakultät Physik/ DELTA, Technische Universität Dortmund, Otto-Hahn-Str. 4, 44227 Dortmund, Germany

b) Physikalische Chemie II, Technische Universität Dortmund, Otto-Hahn-Str. 6, 44227 Dortmund, Germany

c) Institute of Physical Chemistry, University of Muenster, Corrensstr. 28/30, 48149 Münster, Germany

## Report:

The purpose of the experiment HE-3592 was to study changes of the water structure close to the charged surface of micellar colloids. The structural details of this hydration water have been under discussion for a long time and were subjected to different experimental and theoretical studies [1-3]. However, a consensus of the microscopic structure is far from being reached. In order to shed more light into this, we performed X-ray Raman scattering (XRS) spectroscopy measurements on the oxygen K-edge of liquid water and of different solutions of charged micelles for which the cationic surfactant cetyl trimethylammonium bromide (CTAB)

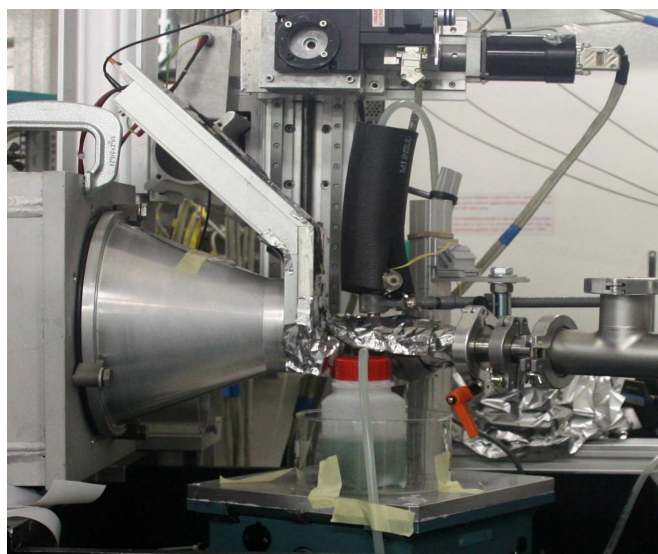


Fig. 1 Percolation setup at ID16.

was used. By increasing the micelle concentration, the ratio of hydration water close to the micelle surface to the bulk water was increased. CTAB was chosen as it is well known to form stable micelles beyond the Krafft point of  $T = 30\text{ }^{\circ}\text{C}$  [4,5] and because it does not contain any oxygen atom which would obscure the XRS signal. With this approach, differences in the local water structure in bulk and close to the charged micelle should be detectable.

The XRS measurements were performed at beamline ID16 using the MAXIPIX detector. In order to avoid radiation damage of the liquid samples a percolation setup was used [6,7]. A picture of this is given in Fig. 1. A flowing jet of the solution was hit by the X-ray beam without employing additional windows. Moreover, this setup allows it to directly determine and regulate the temperature of the liquid to be well

above the Krafft point to ensure the presence of CTAB micelles in solution.

The so-obtained XRS spectra of water and two different CTAB solutions are given in Fig. 2. The solution temperature was set to 40 °C. In order to reveal differences in the spectra due to the presence of hydration water, the signal from the pure water sample was subtracted from that of the two CTAB solutions. The result is depicted in the right of Fig. 1. As is reflected from this plot, there are slight changes at the oxygen K-edge that seem to stem from hydration water, as the spectral differences change with CTAB concentration.

To rule out the sole effect of the free bromide ion which dissociates when CTAB is dissolved, additional solutions of KBr were studied. The data analysis is still in progress.

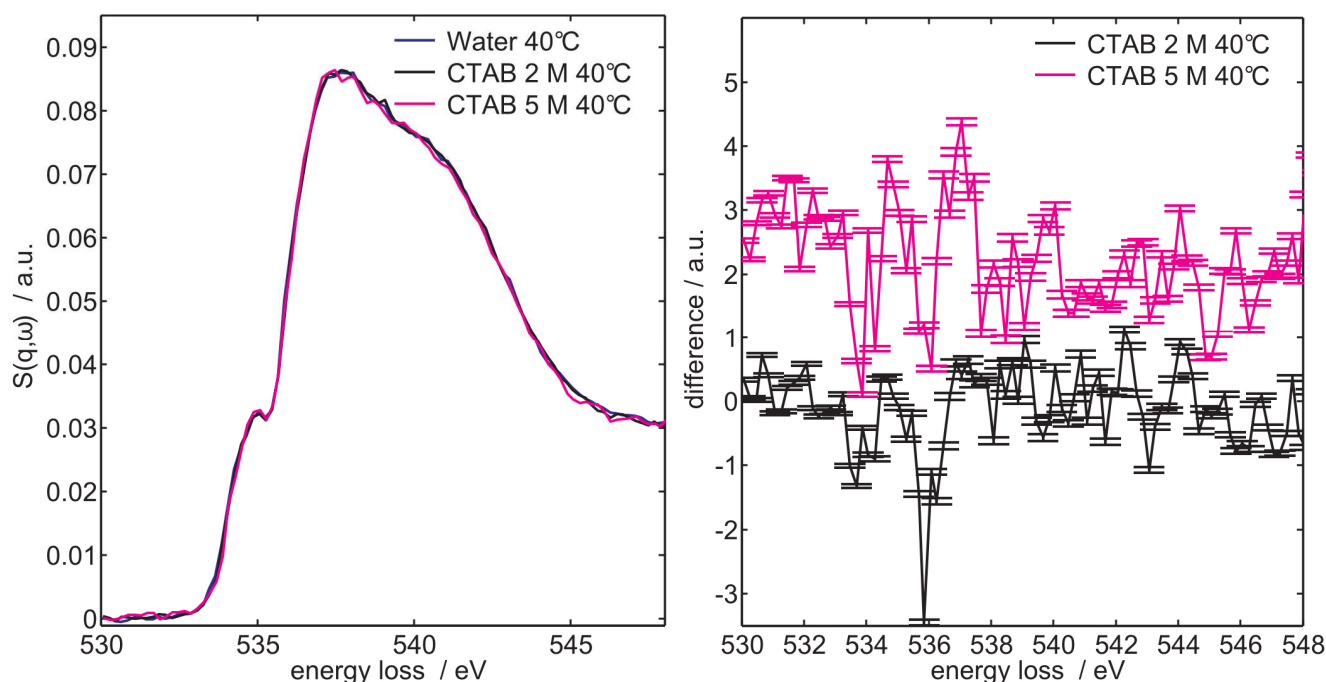


Fig. 2 Left: Oxygen K-edge of liquid water and two solutions of CTAB micelles (concentrations of 2 M and 5 M) at  $T = 40$  °C well above the Krafft point. Right: Difference spectra pointing out the sole effect of hydration water close to the micelles' surface. The difference spectra were shifted vertically for clarity.

To complement this study, calculations of the spectra by using the results of all-atom Molecular Dynamics simulations of CTAB layers in contact with explicit water molecules have been recently conducted. The comparison of the experimental data with the calculated spectra will allow to explore the underlying water structure close to the charged surface of the CTAB micelles.

## References:

- [1] S.H. Lee, P.J. Rossky, *J. Chem. Phys.* **100**, 3334 (1994).
- [2] L. Cheng, P. Fenter, K.L. Nagy, M.L. Schlegel, N.C. Sturchio, *Phys. Rev. Lett.* **87**, 156103 (2001).
- [3] J. Israelachvili, H. Wennerstrom, *Nature* **379**, 219 (1996).
- [4] X. Aury, C. Petipas, R. Anthore, *J. Phys. Chem.* **93**, 7458 (1989).
- [5] T. Wörnheim, A. Jönsson, *J. Colloid Interface Sci.* **125**, 627 (1987).
- [6] T. Pylkkänen, J. Lehtola, M. Hakala, A. Sakko, G. Monaco, S. Huotari, K. Hämäläinen, *J. Phys. Chem. B* **114**, 13076 (2010).
- [7] T. Pylkkänen, *Disordered Matter studied by X-ray Raman Scattering*. PhD Thesis, University of Helsinki (2011).