# ESRF

Experiment title: Design of "green" oxidizing polyphasic microdispersed reaction media. SAXS, ASAXS and kinetics study on microemulsions	Experiment number: SC3231
Beamline: ID2	**Date of experiment**: from: 21/10 to: 24/10/12	**Date of report**: 15/08/12
Shifts: 9	**Local contact(s)**: M. SZTUCKI	*Received at ESRF:*

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Report:

This was a study around the development of surfactants exhibiting catalytic properties, an interesting issue since their localisation at the water-oil interface is likely to increase both the water-oil compatibility and the kinetics of the catalytic reaction. A new class of balanced catalytic surfactants, based on double-chain $[C_nC_mN^+ (C_1)_2]$ (n, m = 6 - 12) ammonium groups electrostatically bound to a **catalytic counter-ion** (MoO_4^{2-}, WO_4^{2-}, $W_2O_{11}^{2-}$, HCO_3^-) able to react with hydrogen peroxide to provide selective oxidizing species (peroxo intermediates, singlet oxygen) have been developed. These double-chain surfactants turn out to be "*balanced*" providing spontaneously three-liquid-phase microemulsion systems at room when mixed with an appropriate organic solvent and water, without addition of electrolyte or alcohol. "*Balanced catalytic surfactants*" thus play the role of surfactant, cosurfactant and catalyst simultaneously, leading to three-phase μem systems with only three components. The resulting balanced triphasic microemulsion exhibit very interesting features to a practical viewpoint (CATASURF CD2I-ANR programme*): fast separation of the 3 phases because of the minimal water-solvent interfacial tension, near zero mean curvature of the interface and maximal cosolubilisation of water and solvent and easy work-up of products and catalyst..

The first part of the proposal was dedicated to static measurement of self-aggregation of this type of surfactant. It tooks a long time to analyze data because the fit procedure should be applied simultaneously on SANS(in black) and SAXS (in red) data to extract coherent set of structural features (see below an example showing a ribbon shape aggregation of (C8C8NC1C1)2)MoO4 in toluene at low concentration, less than 8% to avoid the S(q) analysis. Indeed, the attractive interaction observed for such a system is difficult to describe

analytically. Adjustment using the same set of structural parameter and changing the contrast are used to fit both type of scattering curves). Only few SAXS curves have been analyzed due to a deposition of inorganic compounds of the glass capillary surfaces under x-ray beam. For the experiment we wanted to use the same capillary to improve background subtraction but we were obliged to apply restrictive and timecost procedure to clean and check them after each acquisition. This is a problem observed now quite often when we use inorganic ions.
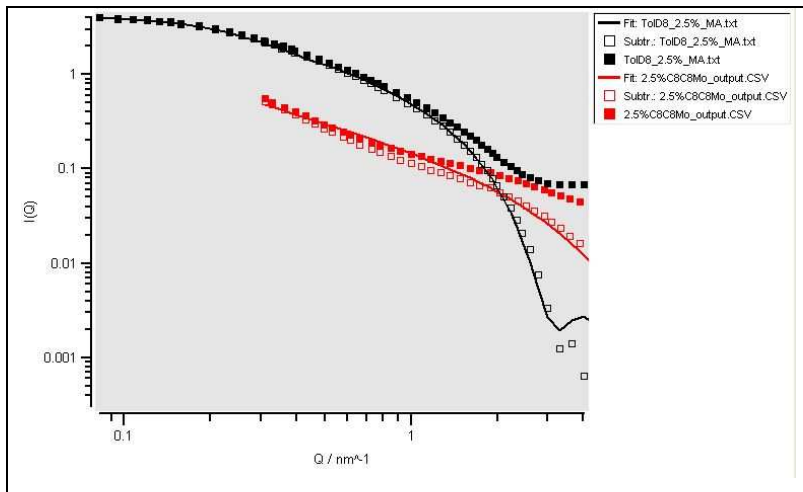
SAXS (red) and SANS (black and obtained from ILL-D22 experiment on similar samples) scattering raw (full) and corrected (empty) data) adjusted using a ribbon-like form factor taking into account packing parameter constrain with various contrast.

Concerning the ASAXS study the experiment was not succesful not because of the experiment itself that was pefect but we were not able to observe any ion condensation because the system was to dilute. Indeed, when concentration of hydrogen peroxide.was increased to have a higher contrast, the system was unstable with the generation of too many gas bubbles, preventing a correct and reproducible data acquisition!

It was the same to follow the kinetic of interfacial topology change when H2O2 was added and we were not able to use the stopped-flow system since organic solvent was used! We tried manually to inject in the capillary cell both fluids but the mixing phenomena was too fast and the only way would have been to decrease the temperature – that force us to modify the set-up of the experiment!

Anyway, a set of analysis concerning the aggregation of this new class of catalytic surfactant in oil will be published quite soon !