	Experiment title: Study of inorganic precipitation in catanionic revesre micelles by time-resolved SAXS	**Experiment number**: SC-1519
Beamline: ID2	**Date of experiment**: from: 24/11/2004 to: 28/11/2004	**Date of report**: 1/09/2005
Shifts: 12	**Local contact(s)**:Stéphanie Finet	*Received at ESRF:*

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Report:

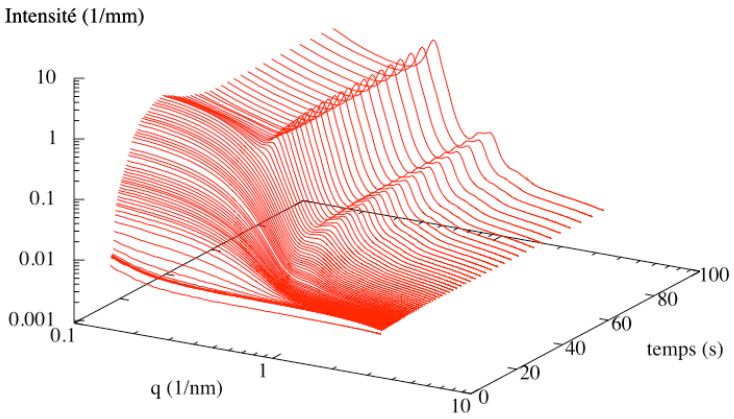
Nanomaterials attracted a great deal of attention during the past few years. A fastly increasing number of papers deal with the synthesis of inorganic nanoparticles of various shapes, size and composition. The mechanism by which those nanoparticles nucleate and grow and the effect of the different experimental parameters is though still very obscur mainly due to the fact that rigorous in-situ experimental datas are lacking. In this experience we wanted to monitore the fast synthesis of gold nanoparticle by in situ time resolved SAXS combining the use of synchrotron radiation and a fast mixing device. This experimental set-up would enable us to look at the very first instants of the reaction and hence get insights in the nucleation and growth mechanism.

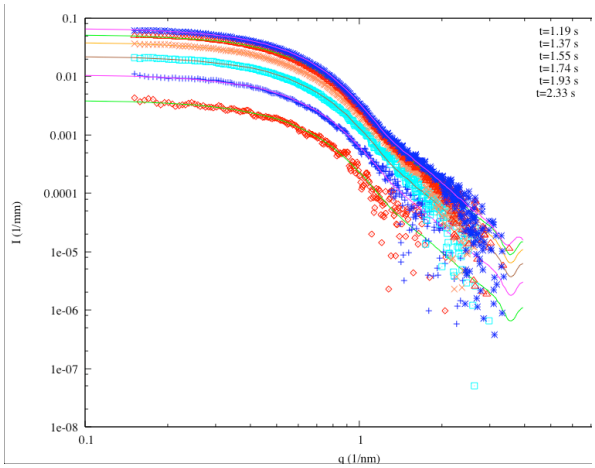
During the allocated official time, experimental problems linked to the use of the stopped with our system prevented us to make reliable measurements. We've tried several times to make proper measurements but at each injection, pieces of joints contained in the stopped flow went into the mixing mechanism which prevented any further utilization unless a complete dismantling, washing and rebuild which takes around 4 hours. Furthemore, the reliability of the datas acquired during this run was questionnable as we did not manage to reproduce the same experiment twice.

After discussing of these problem with our local contact and the ID2 team, they decided to allocate us three extra shifts in April as the problems occuring during our previous experiment was not A new model of stopped flow apparetus which was supposed to work properly with toluene as stated by Bio-Logic (the stopped-flow supplier) was tested at this occasion.

This extra-run went perfectly well and we managed to get reliable, reproduceable datas during the whole allocated time. After this successful try our laboratory bought this new model of stopped flow which will be used for other experiments.

The system used was the synthesis of gold nanoparticles in toluene in presence of capping ligands (carboxylic acid, alkylamine, catanionic surfactants). The previously proposed system (Synthesis of BaSO4 nanoparticles in catanionic reverse micelles) was dropped out because the reverse micellar template had a too high scattering signal as compared to the nanoparticles. The signal of the nanoparticles could hence be hardly isolated. This is not the case in the studied system where the pre-existing template scattering signal is very weak.
The configuration used was a detector to sample distance of 1.5 m and a wavelength of 11.5 keV.
The WAXS camera was not set up at the moment of the experiment and too much time was necessary to set it up. Only SAXS datas were acquired. Typical acquisition sequence involved 120 SAXS patterns in 10 minutes.
We managed to perform 8 acquisition sequences going through different experimental conditions and testing the reproducibility of the experiments.
The figures show a typical sequence obtained and the corresponding fits for the first instants of the reaction.
The 3D diagram shows the evolution of the scattering signal as a fucntion of time.
The spectra were fitted at the absolute scale which enables to get the number of particle and the size distribution.





The first conclusion are that the growth mechanism can be divided in three distincts parts. First, the nucleation of critical nuclei occurs, their number is increasing while their size remains the same. In the particular case shown here, the critical nucleus can be modeled as a 2.4 nm radius sphere. This step is followed by growth of the nanoparticles where their size is increasing. Finally, they self-assemble into super lattice.
These experiment showed too that the nature and concentration of the ligand has a critical effect in the kinetic and final size of the nanoparticle. For example, the organisation into superlattices occurs only when carboxylic acid is used in a sufficient quantity. The chain length of the latter is also important. When alkyamines are used instead, the mechanism is different and nucleation and growth are occuring together which leads to very small more polydipserse nanoparticles.
These first results are really encouraging and original as no in situ experimental datas on the nucleation and growth of nanoparticle are available to date. The proven ability to detect the critical nucleus is of particular importance since many conjectures have been made on its size and shape. Though, to date its in situ observation had never been performed.
The organisation into 3D superlattice is also an original result. This kind of organisation is common in 2D when a nanoparticle film is dried and the monodispersity is sufficient but 3D superlattices had never been observed to the best of our knowledge.
The datas interpretation is, at the moment, being finalized and submission for publication will occur shortly.