



	Experiment title: Mechanism for silica and zirconia nanoparticle growth and final size in compartmented salt-free catanionic nanoreactors	Experiment number: SC-1272
Beamline: ID02	Date of experiment: from: 05/12/2003 to: 08/12/2003	Date of report:
Shifts: 9	Local contact(s): Dr. Theyencheri NARAYANAN	<i>Received at ESRF:</i>
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Report:

The aim of this experiment was to obtain the kinetics of growth of zirconia particles in reverse micelles made of catanionic surfactant. The use of soft colloidal template is a good way to produce silica nanoparticles as described by numerous papers whereas a limited of papers described the synthesis of zirconia nanoparticles in reverse micellar solution.

It is generally assumed that precipitation in reverse micelles occurs through a template mechanism, but if it is often effective for nanospheres, numerous exception are encountered for anisotropic shape. We wanted by this experiment find the key of the precipitation in confined media by varying independantly the parameters that control the microemulsions structure (water activity, pH, surface charge density, interfacial rigidity).

I) set up of filling the syringe and injection procedure

a) wetting properties of octane

The Biologic Stopped flow apparatus has been designed for the use of aqueous solution. After a few tries, we realised that mixing octane solutions in a stopped flow apparatus was not so straightforward and that a carefull tuning of the filling of the stopped flow has to be defined.

As a matter of fact, contamination of one syringe to another occurs very rapidly (more than with water solution), leading to erroneous injection volumes and erroneous composition of the final microemulsion. Furthermore, it has been stated that the opening of the “hard stop” (a valve which is situated at the end of the stopped flow circuit) after a certain period of time leads to the leaking of the capillary and to the whole circuit including the delay lines. Our solutions being essentially made of octane, which has very different wetting properties from water solution, we suspect that our solutions flow easily in the microfluidic device.

Though, we finally found a reproducible method to fill correctly the syringe, to mix the two microemulsions and to avoid a too rapid diffusion from one syringe to another one.

A good method to fill the syringes is the following one :

- All the valve are in the “R” position to isolate the syringe from the mixing chamber. The reservoir of the first syringe is filled with a sufficient quantity of microemulsion (typically 7mL)
- The valve is still turned in the “R” position and part of the reservoir syringe is put in the injection syringe
- Part of the solution is re-injected in the reservoir syringe. The two previous steps are repeated several times to ensure the absence of bubbles in the injection syringe.
- The same procedure is applied to the other syringes.
- Then, the valve of the syringe containing octane (which is used to wash the circuit) is put on the “C” position and some octane is injected in the circuit.
- Then the valve of the syringe containing octane is put on “C” to isolate it and the valve of the two other syringes are put on “R” position.

Since while the hard stopped is open the octane solution flow away from the capillary and the circuit, it is not essential to fill the delay lines with octane before starting the mixing. To ensure that the good quantities are injected during acquisition, relatively high quantities of the reactants are injected via the software just before the acquisition starts.

A typical injection procedure was the following :

- 400 μ L of each reactants is injected in the stopped flow device
- a second injection, identical to the one which will be studied is computed
- finally, the “real” injection is performed and the SAXS patterns acquisition system is triggered;

When all those precautions are taken, mixing sequences and acquisitions can be performed in a reproducible manner.

At the end of the acquisition time, the valve of the syringe are put on “R” to avoid interdiffusion.

b) cleaning of the capillary

A last problem remains, after an acquisition sequence, the SAXS pattern of the clean capillary can be pretty hard to recover. To recover a clean capillary, a 2 ml of octane were first injected in the capillary. Afterwards, a sulfuric acid solution (3% in weight) is injected and the cleaning process is let to occur for 10 minutes. A last injection of octane enables the recovery of the clean capillary SAXS spectrum.

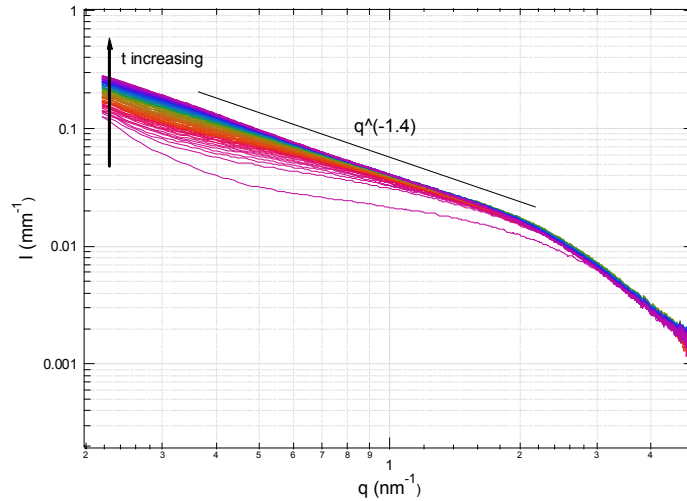
After all those experimental procedures were set up, reproducible experiments have been performed but the filling and washing procedures are time-consuming and part of the allocated time has been used for the set-up of these procedures.

II) Precipitation of Zirconia in reverse microemulsion

- system studied:

The microemulsion chosen for the experiment was a mixture of a true catanionic (octylamine + octanoic acid in 1/1 proportion), octane as oil and a water core. For this first experiment, the concentration in catanionic was 0.4M and the water to surfactant ratio was 2.

The Zirconium propoxide is dissolved in anhydrous octane under an argon atmosphere to prevent hydrolysis prior to reaction. The 3 different syringes were filled in as follows : anhydrous octane in S1, catanionic microemulsion in S2, propoxyde zirconium solution in S3. Great care was taken during filling of the alcoxyde solution to completely purge to stopped flow apparatus with dry argon, the latter being extremely sensitive to moisture.



A first acquisition sequence was then started as shown on the graphics above. We can see that a $q^{-1.4}$ regime is taking place as the reaction occurs. The reaction is fast and the final equilibrium state is obtained after less than 1 minute. From this experiment, we can presume the presence of fractal aggregates of dimension 1.4. Though the precise structure of those aggregates are still under investigation.

After this first experiment, the recovery of a clean capillary was difficult to obtain. Furthermore, uncontrolled precipitation of the zirconium alkoxyde occurred in the interior of the stopped flow apparatus leading to erroneous injection volumes. Several attempts to reproduce the first acquisition sequence by emptying all the syringes and a careful refill of the latter under dry argon failed. After 4 shifts, we decided to investigate barium sulfate precipitation in cationic reverse micelles to have a model system to follow a precipitation in a cationic system. We presume that the reactivity of the inorganic precursor was too high (zirconium alkoxydes are extremely sensitive to moisture and cannot bear even a short contact with air). A good way to tackle this problem would be to use less reactive precursors such as acetylacetonate or zirconium glycolates and to use diluted solutions. All the microemulsions were characterized during this part of the experiment.

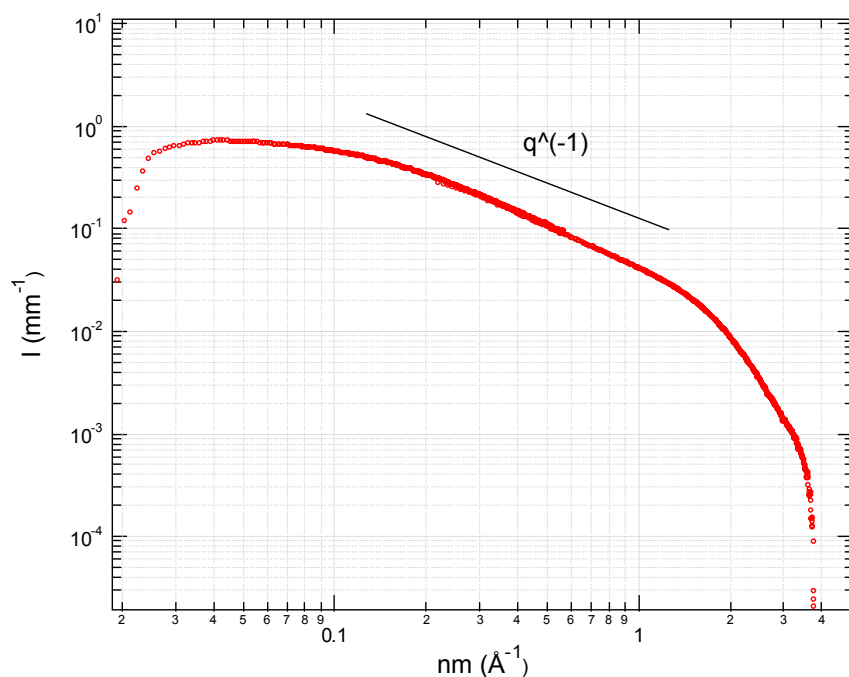
II) Precipitation of barium sulfate in cationic reverse micelles

Experiments were performed with 0.4M cationic (a mixture of octylamine and octanoic acid) solutions in octane. The water core of the micelles consists of either BaCl_2 or Na_2SO_4 at 0.1M or 0.5M. For each experiment, the BaCl_2 microemulsion is loaded in one of the syringes, the corresponding Na_2SO_4 microemulsion is loaded in another syringe, the last syringe is dedicated to octane used for washing the whole apparatus after injection.

Different parameters have been varied during those experiments.

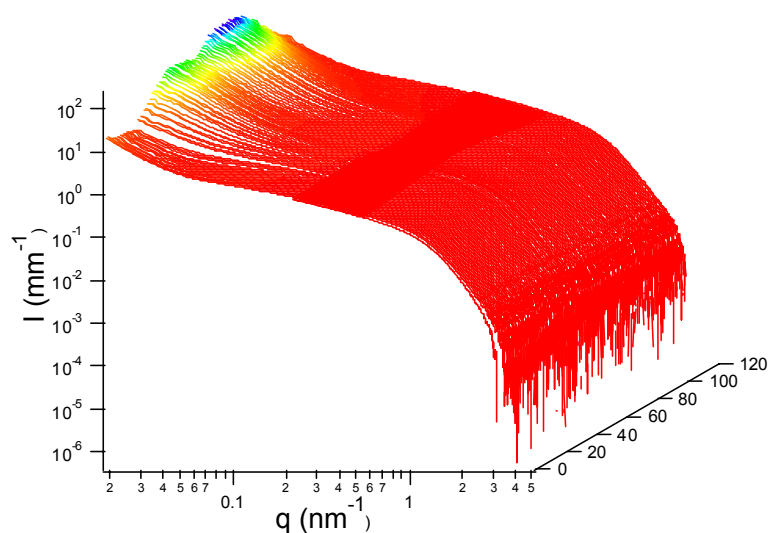
- 1) The influence of the volume ratios of the different microemulsions on the growth of the nanostructured material has been studied. The surface charge of the particles can be varied in this way by a variation of the ion adsorption at the surface. Moreover the ion adsorption on the particles should depend on the nature of the salt.
- 2) Variations in the concentration of the salt has also been investigated.
- 3) Finally two different microemulsions have been used, the first one was made of an equal quantity of amine and acid (true cationic) whereas a slight excess of amine was present in the second case.

A typical SAXS pattern of a microemulsion is shown below :



All the microemulsions showed similar patterns and a wormlike micellar structure can be inferred from the q^{-1} Behaviour of the scattered intensity.

A typical $I(q,t)$ pattern is shown below :



The reaction is followed from 0.016 to 900 s after injection for salt concentration of 0.5M, a amine to acid ratio of 1 and a 50/50 mixing ratio. After mixing the intensity at low q decreases until 1.5 s and increases again from 1.5s to 700 s.

The data treatments on the other compositions are in progress at the moment.

All those sequences obtained with barium sulfate will allow us to obtain the reactivity in cationic reverse microemulsions.

Conclusion

Because of the wetting properties of octane, and the different behavior of octane solution in the stopped flow apparatus by comparison to water solution, a large part of the allocated time has been used for the set up of the filling of the syringe and of the injection sequence.

The high reactivity of the zirconium precursor solution and the adsorption of zirconia on the capillary, did not allow us to perform the kinetic study of the zirconia precipitation. The synthesis conditions of the precipitation has to be changed by using a less reactive zirconium precursor as acetylacetonate and more diluted solutions to avoid adsorption on capillary.

We characterised the precursor solutions involved in this synthesis and decided to follow barium sulfate precipitation in catanionic reverse microemulsions to optimise the allocated beam time. This synthesis will permit to extract the key parameter of the synthesis in catanionic media. The results can be used for zirconia precipitation.

With Barium sulfate, we see that the most important parameter is the amine to acid ratio. The data treatments are in progress, and complementary experiments such as TEM, conductivity measurements and SANS are performed to complete this study. Most of the problems encountered during this experiment were due to the difficulty to use the stopped-flow apparatus with our solutions and to design efficient and reproducible mixing procedures. Though, we've got the feeling that most of the problems have been solved during the allocated time and that these experiments are feasible. All the more, we managed to characterise numerous microemulsions and to vary a range of parameters in the inorganic precipitation in catanionic reverse micelles.