Experimental report

31/03/2017

Proposal: 9-10-1511 **Council:** 10/2016

Title: Droplet microemulsions confined tocylindrical nanochannels

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Gerhard FINDENEGG

Experimental team: Albert PRAUSE
Anja HOERMANN

Local contacts: Viviana CRISTIGLIO

Samples: SiO2
hexanol / C6H13OH
sodium tetradecyl sulfate / C14H29NaO4S
tetradecyltrimethylammonium bromide / C17H38BrN
tetradecyldimethylamine oxide / C16H35NO
decane / C10H22

Instrument	Requested days	Allocated days	From	To
D16	5	5	10/02/2017	15/02/2017

Abstract:

The structural arrangement of colloids in confinement is a generally important topic that will be addressed here by employing rather monodisperse microemulsion droplets in well defined silica pores (SBA-15). In these experiments the size and surface charge of the microemulsion droplets will be varied systematically, as well as the pore size in order to achieve comprehensive insights into how these parameters affect the incorporation of microemulsion droplets into such pores. These experiments are both of fundamentally high interest, as these are very well defined model systems, but also relevant as the solubilisation of oil in the presence of pores is of central importance for processes like tertiary oil recovery or soil decontamination. SANS is uniquely qualified for this study as by contrast matching of the silica pores one can solely focus on the structural arrangement of the microemulsion droplets. From the analysis of the scattering patterns we will gain comprehensive insights into how this confinement affects the structure and arrangement of the soft microemulsion droplets.

Droplet microemulsions confined to cylindrical nanochannels

Experimental report for experiment 9-10-1511 at D16 (Feb. 10–15, 2017)
Berlin, March 31, 2017

Experimental setup and samples We studied the behaviour of oil in water (O/W) microemulsion droplets (ME) confined to cylindrical pores of SBA-15 silica. TThe ME droplets were composed of *n*-decane as oil, tetradecyldimethylamine oxide (TDMAO) as surfactant and 1-hexanol as cosurfactant, where for some samples 5 mol% of the TDMAO were substituted by ionic surfactant. The investigated system has a large set of parameters. According to this, we focused on the variation of charge and pore size of SBA-15, charge and droplet size of MEs and also the filling fraction of the pores with MEs.

Small-angle neutron diffraction (SAND) measurements were performed at the instrument D16. We used a neutron wavelength of 4.55 Å and a single detector configuration with an angle of 0 ° and an optimized collimation to resolve the (11) and (20) Bragg reflexes of the pore lattice. The explored q space was in the range of 0.03–0.32 $Å^{-1}$.

Mainly, the sample preparation was carried out with a H_2O/D_2O mixture that matches the scattering contrast of our SBA-15 silica materials. This contrast matched conditions were necessary to observe only the scattering contribution of surfactants and oil (droplet contrast). For a few samples we matched the oil with a *n*-decane-h_{22}/*n*-decane-d_{22} mixture as well (film contrast of the ME droplets). For the preparation we pre-wetted the silica material with the H_2O/D_2O mixture. Afterwards the corresponding amount of the desired ME stock solution for one filling fraction was added to the silica suspension. The suspension was mixed carefully and the pH was checked and adjusted if necessary.

The indication of samples follows the sequence of name of SBA-15 silica, pH, short name of ME (increasing number with increasing droplet size) with or without additional charge of ME (p/m stands for 5 % positively/negatively charged surfactants), filling fraction of ME and the contrast condition (HD: droplet contrast with silica contrast match; FC: film contrast). For example the sample AP10_9_ME1-0_f2_HD consists of AP10 (name of the SBA-15 batch) as SBA-15 with desired pH of 9. The used ME, ME1-0 is the smallest uncharged ME with the second filling fraction. The scattering length of the solvent was adjusted to the contrast match point of silica.

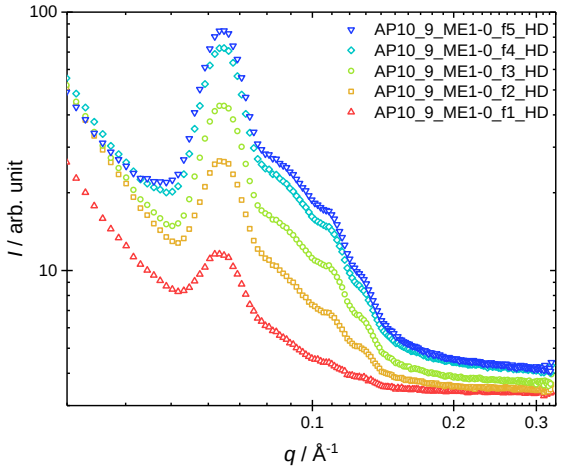

Figure 1: Variation of filling fraction of the pores. Fractions f1 to f5 are filling ratios of ME droplet volume to pore volume of 10, 30, 60, 90, 120 %.

Variation of filling fraction We varied the filling fraction of the porous silica. Five different ratios of overall ME droplet volume to pore volume between 10–120 % (f1–f5) were adjusted. In figure 1 we can see an increase in diffuse scattering. Also the intensity of the (10) Bragg reflex shows a large increase from f1 to f5.

Variation of charges The charge conditions were varied by adjusting the pH or replacing TDMAO with the similar ionic surfactant sodium tetradecylsulfate (TDS) as anionic or tetradecyltrimethylammonium bromide (TTAB) as cationic surfactant.

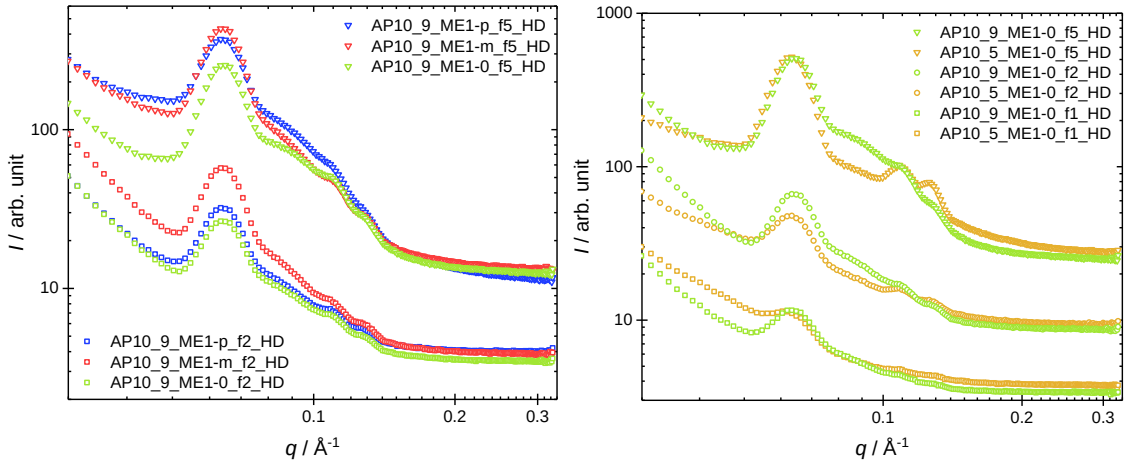

Figure 2: On the left hand side the charge of the ME was varied and plotted for two filling fractions. The right hand side shows the pH variation which are displayed for three filling fractions.

Figure 2 shows the variation of ME charge (left hand side) and the variation of surface charge of the silica material via the pH (right hand side). The presence of a ME charge leads mainly to the diffuse scattering and has no a pronounced affect to the intensity of the Bragg reflexes. In contrast to the ME charge the pH variation has a larger influence on the Bragg intensities and a moderate effect on the diffuse scattering at higher filling fractions.

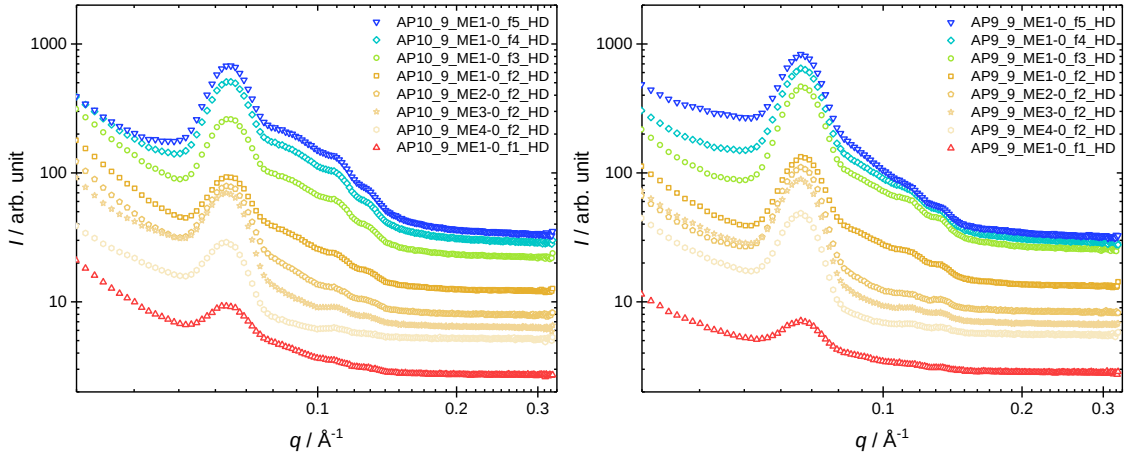

Figure 3: The left hand side shows the series of filling fractions in AP10. For filling fraction f2 different ME droplet sizes (ME1–ME4, orange symbols) were used to investigate the influence of droplet size. On the right hand side the same plot with smaller pore sizes is displayed.

Variation of sizes In the experiment we varied two kind of sizes: the ME droplet size and the SBA-15 pore size. The ME droplet size was varied by preparing MEs with 1-Hexanol as cosurfactant. We adjusted the ME droplets to 4 different radii in the range of 3–6 nm (ME1–ME4). For the pore size variation two different SBA-15 materials were synthesised. The pore diameter for AP9 and AP10 were approximately 7 nm and 8 nm.

The influence of droplet size is shown in figure 3 with a decrease in diffuse scattering for increasing droplet sizes.

Variation of contrast condition In addition we adjusted the contrast conditions for the oil inside the ME to the contrast match point of the silica and water. This results in scattering from the surfactant layer only (film contrast; short: FC).

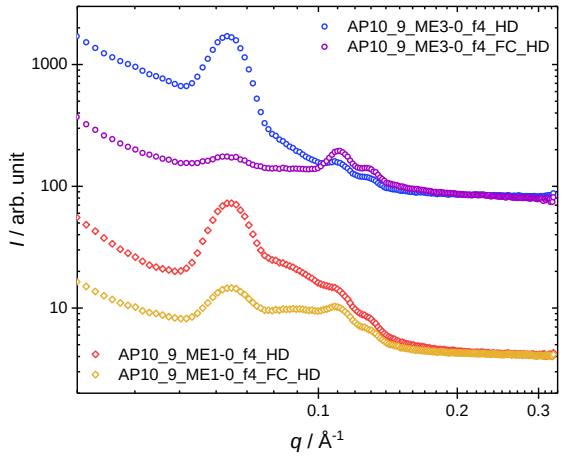

Figure 4: Film contrast conditions for one filling fraction of small ME droplets (ME1) and large ME droplets (ME3).

The film contrast condition has a pronounced effect on the diffuse scattering (fig. 4). The ratios of Bragg intensities were changed. The (10) reflex intensity goes down while the intensities of (11) and (20) reflex show a moderate increase.

Data analysis The scattering intensity will be divided into 2 coherent scattering contributions and the incoherent background. The first part the diffuse scattering contribution will be fitted with a model like Teubner-Strey. The second part the Bragg intensities will be fitted with a cylindrical or cylindrical shell form factor. From these informations we want to find out which contribution and shape the ME droplets inside the pores could have. In general, the outcome of this experiment was very successful and has delivered very valuable insights into this complex system of inorganic pores with contained microemulsion droplets.