ESRF	**Experiment title:** USAXS investigations on the preparation of porous silicas using structure directing devices	**SC 595**
ID02A	**Date of experiment**: from: 26-01-2000 to: 31-01-2000	**31-8-2000**
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Report:

Porous silicas as models for biogenic silica in diatoms were prepared using organic molecules as templates. Because the sizes of the pores in diatoms are covering a very large range (from 10 micron down to a few nanometers[1]), to observe these pores (and their precursors in the reaction mixture) the combination of USAXS and SAXS (for recent SAXS results see ref.4) are necessary to investigate appropiate pores and pore formation in both diatoms and the related silica models.
During the USAXS experiments the preparation of porous silicas has been investigated using a rotating thermostrated cell containing the reaction mixture. The development of the silica-template intermediates could be studied "in situ" applying successive scans with the Bonse-Hart camera (scanning time 10 -15 min).
Results:

a. No template. Because at our reaction conditions porous silica is formed also without templates, we studied the aggregation of silica at pH = 4 and at both 25 and 90 °C. As expected from the extrapolation of our previous SAXS experiments at these systems[2], growing aggregates were observed in the 40 - 300 nm range.
b. According to recent reports, the hydrophobicity of templates is very important and therefore polyglycol ($HO\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ with $n = \pm 45$) was chosen as the first template. During the

preparation of the silica-polyglycol hybrids at pH = 4 and at both 25 and 90 °C, a gradually shift in scattering intensity by the intermediates was observed from the 40 - 70 nm to the 600 - 4000 nm range. Moreover, the final scattering curve showed periodic "ripples", typical for the scattering by monodisperse or very slightly polydisperse spheres, observed (but at a much smaller length scale!) at precipitated silicas[2]. The size of these silica-polyglycol particles, however, is much bigger than might be expected from the size of the polyglucol polymers. We assume therefore that, similar to results obtained by Takahashi c.s.[3], silica has triggered the formation of polyglycol-micelles at the micrometer scale, and these micelles are the templates for the formation of very big silica particles.

c. To change to a more hydrophilic system, similar experiments were performed using polyethene-imine ($(CH_2\text{-}CH_2\text{-}NH)_n\text{-}H$ with n = ± 5000). Contrary to polyglycol, at similar experimental conditions this much bigger polymer produced relatively small and non-structured scattering curves between 40 and 300 nm. Although the scattering intermediates, according to the length scale, must be much bigger compared to the silica aggregates obtained without templates, probably no micelles were formed now and the growth of silica particles was steered by single strands of the polymer.

d. In diatoms specific proteins are used as templates. Because up to now no diatom proteins are available, two other well-known proteins (the enzymes Myoglobine and Horseradish Peroxidase) were applied. The scattering patterns were again very different, even between the two proteins. During the reaction Horseradish peroxidase slowly developed a rather sharp band around 50 nm, but Myo-globine showed only during the first hour a rather weak and irregular band between 40 and 150 nm, in the second part replaced by a rather strong double-peaked band between 2 and 3 micron. Because the average radius of both proteins is only 4.5 nm (Myoglobine) and 3.5 nm (Horseradish peroxi-dase), probably the growing silica is templated by clusters (?) of these proteins, with the smallest one forming by far the biggest particles.

e. In previous experiments[4], SAXS spectra of the dried and cleaned frustules (= silica skeletons) of diatoms were recorded. Now the porous structure of the frustule a Biddulphia species has been inves-tigated with USAXS, using some powdered frustule on Scotch tape in the rotating cell. The strongly scattering porous silica showed at least 6 different peaks between 60 and 3000 nm, to be attributed to structure factors due to interactions between different sets of pores and similar to the structure factors shown in SAXS pattern of mesoporous silica (for example the MCM-silicas), only at a larger scale.

References:

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3. R.Takahashi, K. Nakanishi and N. Soga, "Aggregation behaviour of alkoxide-derived silica in sol-gel process in presence of poly(ethylene oxide)", J.Sol-Gel Sci.Techn., **17** (2000) 7-18

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