# Experimental Report

18/10/2013

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| **Proposal:** | **9-11-1621** | **Council:** | 4/2012 |
| **Title:** | Hydration pressure in nonionic block copolymer systems | | |

**This proposal is a new proposal**

**Researh Area:** Soft condensed matter

**Main proposer:** **GRILLO Isabelle**

**Experimental Team:** SCHMITT Julien
IMPEROR-CLERC Marianne

**Local Contact:** GRILLO Isabelle
CRISTIGLIO Viviana

**Samples:** pluronic P123, F127 in D2O
HCl, NaCl, dodecane

| **Instrument** | **Req. Days** | **All. Days** | **From** | **To** |
|---|---|---|---|---|
| D16 | 5 | 5 | 21/11/2012 | 26/11/2012 |

**Abstract:**

Mesoporous materials have attracted a lot of attention over the past decade due to the high potential applications such as heterogeneous catalysis, separation processes and novel applications in optics and electronics. The pore diameter (typically from 2 to 30 nm) and the wall thickness are the major parameters which influence possible utilization of mesoporous materials. The pore size is directly linked to the diameter of the templating micelles. The wall thickness – from which depends the solidity of the material – is more difficult to control. A recent paper proposes a new approach, based on the molecular force balance, to explain qualitatively and in some simple cases quantitatively the wall thickness of mesoporous materials obtained by a sol-gel route. The model represents correctly the data for charged surfactants, but failed to explain the results for nonionic Pluronic templates. One reason could be the hydration pressure that is not known for pluronic. Consequently, we propose to measure the hydration pressure as a function of the relative humidity for two Pluronic molecules using the humidity chamber available on D16.

# Hydration pressure in nonionic bloc k copolymer systems

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Experiment 9-11-1621, D16, 21-26/11/2012

Mesoporous materials have attracted a lot of attention over the past decade due to widespread applications such as heterogeneous catalysis, separation processes and novel applications in optics and electronics.

Several real time experiments carried out on D22 at the ILL since 2003 [1-3] and NIST [4] have allowed one to identify the different steps and mechanisms involved in the formation and growth of mesoporous materials. This involves the formation of a lyotropic surfactant-based liquid crystal that acts as the structure directing agent or template. In the first minutes, during the hydrolysis of the inorganic precursor, the micelles of P123 remain spherical. At the end of the hydrolysis, organic-inorganic micelles are formed where the silica species are placed in the hydrophilic shell which induces a shape transition from spherical to cylindrical. These cylinders aggregate according to an hexagonal lattice. Following a sol-gel process, the condensation of the silica occurs in the aqueous phase between the templating cylinders to form the wall of the hybrid material.

The pore diameter (typically from 2 to 30 nm) and the wall thickness are the major parameters which influence possible utilization of mesoporous materials. The pore size is directly linked to the diameter of the micelles. The solidity of the material depends on the wall thickness but is more difficult to control.

A schematic representation of the hybrid phase organization in presented in Figure 1. The distance *a* between adjacent micelle is determined from the first order Bragg peak position $q_0$ according to: ¯ and

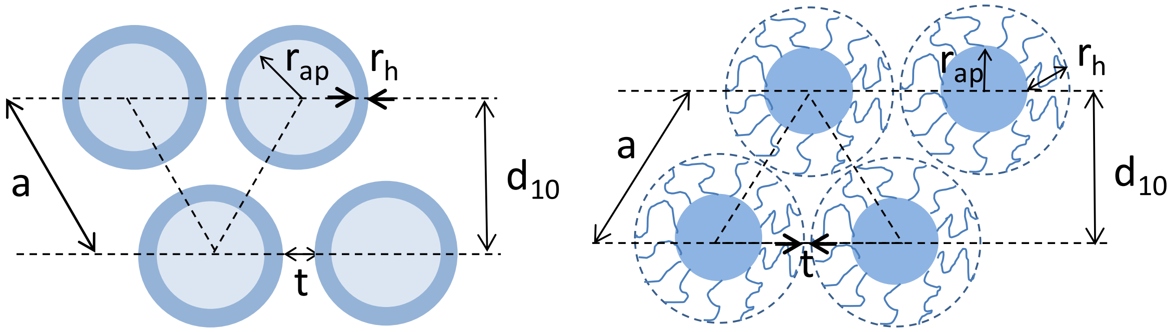

**Figure 1: Schematic representation of the hybrid phase structure. *R* is the total radius of the micelle. *t* is the silica wall thickness and *a* is the micellar inter-distance. Left: ionic surfactants; right: nonionic pluronic molecules.**

A recent paper [5] proposes a new approach to explain qualitatively and in some simple cases quantitatively the wall thickness of mesoporous materials obtained by a sol-gel route. The evaluation of the wall thickness is based on molecular force balance that minimizes the free energy between adjacent micelles. The molecular interactions are separated into three additive terms and consist of two repulsive terms (hydration and electrostatic) and one attractive term (van der Waals).

Figure 2 (left) shows the force balance in the case of a charged surfactant molecule CTAB. The foreseen wall thickness is 16 Å. In [1] the Bragg peak positions is found at 0.134 $\text{Å}^{-1}$, corresponding to a lattice parameter of 54 Å. With a radius of 20 Å for the CTAB micelle, the experimental wall thickness is 14 Å in very good agreement with the theoretical model.

Figure 2 (right) presents the force balance for the nonionic triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$). The calculated wall thickness is 19 Å, whereas the experimental distance $t$ between adjacent micelles varies between 6 and 10 Å [2,6] according the synthesis route, but the wall thickness is much larger, or the order of 50 Å, due to the condensation of the silica inside the large and hydrated polar shell made of EO groups. The case of P123 seems here to reach a limit of the theoretical model. However a major question remains the hydration pressure and the values of the decay length $\lambda$ and osmotic compressibility $\Pi o$. For the nonionic molecules, experimental data are scarce [7] compared to those available for charged surfactants and lipids [8]. A small variation of $\Pi o$ has a strong effect on the final force balance and thus on the predicted wall thickness and could be at the origin of the discrepancy between model and experiment.

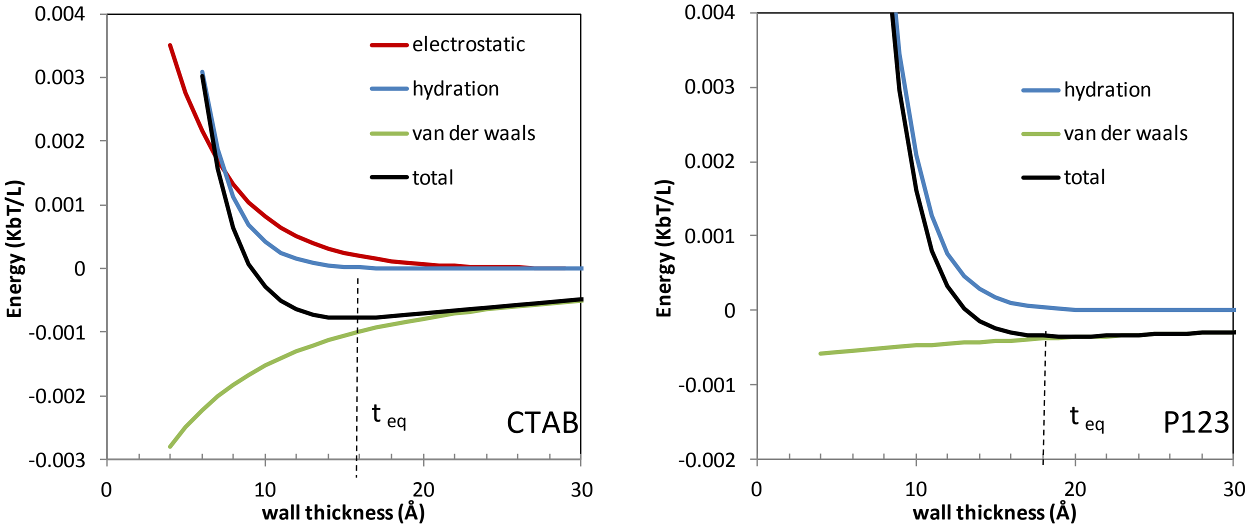

**Figure 2: (Left) Force balance for the charged surfactant molecule CTAB. (Right) Force balance for the nonionic triblock copolymer P123.**

During the experiment we aimed to measure the hydration pressure of the Pluronic P123 in water at two temperatures, 25°C and 40°C and to test the influence of HCl, NaCl and of the swelling agent dodecane to reproduce the synthesis conditions described in [2] using the humidity chamber available on D16.

However, we face a serious problem during the sample preparation. Indeed nonionic surfactant in solution ran down the vertical silicium wafer in a much faster time scale than the one required for the equilibration.

To overcome the problem, we tried to stick the sample between two thin silica wafers. We observed some evolution of the Bragg peak position, but the experiment was not reproducible. The apparent equilibrium sate was depending on the initial pluronic concentration. In this relatively confined environment, the sample hydration takes several days or even months.

However, the hydration pressure of nonionic surfactant molecules remains a challenging question. To repeat the experiment in good conditions, we have two possibilities:
- to find a substrate on which nonionic does not flow,
- to work with a horizontal support and use reflectivity or grazing incidence to determine the Bragg peak positions.

References
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