

Evidence for Vesicle Formation during the Synthesis of Catanionic Templated Mesoscopically Ordered Silica as Studied by Cryo-TEM

Svetlana Pevzner,^{†,‡} Oren Regev,^{*,†,§} Anna Lind,^{||} and Mika Lindén^{*,||}

Department of Chemical Engineering, Ben-Gurion University of the Negev, Box 653, 84105 Beer-Sheva, Israel, Department of Chemical Engineering, Negev Academic College of Engineering, Box 45, 84100 Beer-Sheva, Israel, Department of Chemical Engineering and Chemistry, Technical University of Eindhoven, Box 513, 5600MB Eindhoven, The Netherlands, and Department of Physical Chemistry, Åbo Akademi University, Porthansgatan 3-5, 20500 Turku, Finland

Received October 14, 2002; E-mail: mlinden@abo.fi, O.Regev@tue.nl

The unique properties of inorganic, mesoporous materials templated by supramolecular surfactant aggregates include a narrow pore size distribution, high specific surface area, high specific pore volume, and a tunable pore diameter. The mechanism of formation of these materials is now quite well understood, due to careful in situ studies, as recently reviewed by Patarin et al.¹ There is now some agreement in that the early stages of formation involve (i) hydrolysis of the silicate precursor, (ii) condensation of silicate units leading to oligomeric/polymeric silica, (iii) the binding of surfactant to oligomeric/polymeric inorganic species paralleled by a cooperative self-assembly into a mesoscopically ordered inorganic-surfactant phase concentrated in surfactant and in silicate polyions. The phase-separation process increases the local concentration of inorganic species facilitating further condensation into a rigid framework. Much less work has been devoted to the use of surfactant mixtures as structure-directing agents, and only a few reports^{2,3} concern the use of a mixture of anionic and cationic surfactants for this purpose. However, catanionic surfactant mixtures are known to form extended rodlike micelles already at low concentration and also to readily form lamellar phases in aqueous solution. Furthermore, the formation of vesicles is often observed in these systems as well. These effects are connected to the charge neutralization by ion-pairing coupled with the release of hydration water and screening, which leads to a pronounced increase in the surfactant packing parameter, to values higher than that of the individual surfactants.¹⁰ Furthermore, nonideal mixing effects may also be involved in the stabilization of vesicular structures in these systems. Recently, we have used a mixture of oppositely charged surfactants, cetyltrimethylammonium bromide, CTAB, and 1-alkyl carboxylates, as structure-directing agents in the room-temperature synthesis of mesoscopically ordered silica under alkaline conditions.³ A 2D hexagonal-to-lamellar phase transition was observed with increasing decanoate (DA)/CTAB molar ratio by X-ray diffraction (XRD), in agreement with the expected increase in the surfactant packing parameter. Furthermore, very extended thin silica sheets of uniform thickness were observed for calcined samples by transmission electron microscopy (TEM).^{3b}

To study the possible formation of silicate-surfactant vesicles during the course of the reaction, an in situ cryogenic-TEM⁴ (Cryo-TEM) study was performed on a selected aqueous system, where the lamellar phase dominates. In Cryo-TEM one studies the supramolecular structure in solution by vitrifying in liquid ethane a drop of solution on a TEM grid without staining or drying the sample.⁵ The sample is further imaged under liquid nitrogen

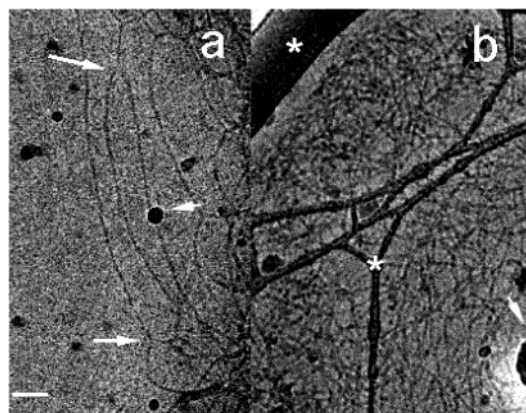


Figure 1. Cryo-TEM images recorded after a reaction time of 85 s for catanionic templated silica, showing (a) micellar junctions (long arrows) and (b) threadlike catanionic surfactant-silicate micelles. The short arrows and stars indicate ice and film support, respectively. Bar = 50 nm.

temperature in the TEM. Cryo-TEM has previously been shown to give very detailed information on the formation mechanism of cationic surfactant-templated mesoscopically ordered, MCM-41-type silica.⁶ The synthesis has been described in detail in ref 3. The final molar composition was 157/3/0.15/1/0.062/1.48 H₂O/NH₃/CTAB/TEOS/DA/toluene. The reaction was quenched to prepare cryo-TEM samples by vitrification at different points in time after addition of the TEOS. A combination of two images recorded after a reaction time of 85 s of different parts of the sample is shown in Figure 1. Very extended disordered rodlike micelles, with contour lengths exceeding 1 μ m, are observed throughout the sample. The micelles are interconnected in junctions,⁷ which are indicated by arrows in Figure 1a. Some other areas in the grid show a more developed network formation (Figure 1b).

No evidence for mesoscopic order can be observed by XRD at this stage, in agreement with the TEM results. However, at a reaction time of 100 s a mixed hexagonal and lamellar phase has been observed by in situ XRD.^{3a} This is clear evidence for the fact that surfactant-silicate micelles serve as precursors also for the lamellar phase in reactions carried out at surfactant concentrations lower than those needed for lyotropic mesophase formation. Corresponding Cryo-TEM images recorded for samples vitrified after a reaction time of 210 s are shown in Figures 2 and 3. The organization is now clearly evident, and again long rodlike micelles are observed together with a large number of junctions. Interestingly, some catanionic surfactant-silicate vesicles are clearly seen in Figure 2, with a lamellae thickness between 6.5 and 8 nm. This is the first time that true vesicles have been imaged in situ for developing inorganic-surfactant systems.

[†] Ben-Gurion University of the Negev.

[‡] Negev Academic College of Engineering.

[§] Technical University of Eindhoven.

^{||} Åbo Akademi University.



Figure 2. Cryo-TEM image recorded after a reaction time of 210 s for cationic templated silica. The arrow indicates a vesicular cationic surfactant-silica structure. Bar = 100 nm.

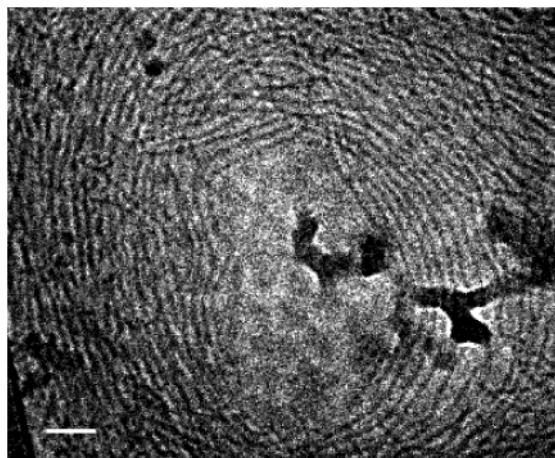


Figure 3. Cryo-TEM image recorded after a reaction time of 210 s for cationic templated silica. Bar = 50 nm.

It is interesting to note that while elongated silicate-surfactant micelles can be observed already at an early stage of the reaction, vesicles can only be observed at a later stage. There are no indications for the presence of vesicles in the aqueous cationic surfactant solution prior to the addition of TEOS. Therefore, one can conclude that it is the presence of silicate oligomers in the system that drives the vesicle formation. The decrease in the interfacial curvature with time is also evident from the formation of a lamellar phase, detected later by XRD.³ It has previously been shown⁸ that strongly adsorbing ions can induce vesicle formation in nonstoichiometric cationic-anionic surfactant mixtures, due to an enhanced charge screening. Negatively charged silicate polyions will readily form at the synthesis pH used, around 11, which will interact strongly with the still net-positively charged surfactant assemblies. The effect of the decrease in the concentration of “free” surfactant with time should, however, not be overlooked, since

vesicle formation is often observed in very dilute surfactant solutions.⁹ Furthermore, the CTA^+/DA^- ratio in solution may also decrease with time if CTA^+ has a stronger affinity for the silicate polyions than the CTA^+-DA^- ion pair. However, the very long entangled micelles observed already before there is any sign of vesicle formation is suggested to be a result of the use of a mixture of cationic and anionic surfactant as structure-directing agents, which indicates that changes in the surfactant ratio during the synthesis may not be the determining factor for vesicle formation.

Another interesting parameter in the synthesis is the presence of toluene. Hydrophobic additives are often used to increase the diameter of the hydrophobic portion of the inorganic-organic supramolecular assembly, since they will preferentially be solubilized inside the micellar aggregates. Comparing Figures 1 and 3, respectively, an increase in the micellar diameter from about 4 to about 7 nm is observed. This observation is well in line with previous results obtained from in situ XRD measurements on the same system, where it was seen that a large portion of toluene was solubilized after the silicate-surfactant mesophase had formed.^{3a} Toluene has been shown to be solubilized both in the core and in the palisade layer of CTAB micelles and may partially also contribute to the stabilization of vesicles by influencing the value of the packing parameter of the supramolecular assembly. To conclude, the formation of vesicles during the development of a surfactant-templated inorganic mesophase has been imaged for the first time. The employed mixture of an anionic and a cationic surfactant as structure-directing agents facilitates the formation of vesicles in combination with the decrease in interfacial charge density upon adsorption of negatively charged silicate polyions. Furthermore, toluene is continuously incorporated into the silicate-mixed surfactant assemblies during the formation of the mesophase, in agreement with earlier conclusions based on in situ XRD results.^{3a}

Acknowledgment. The Finnish Technology Foundation, TEKES, is gratefully acknowledged for financial support. Dr. Stefan Karlsson is thanked for valuable discussions.

References

- (1) Patarin, J.; Lebeau, B.; Zana, R. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 107 and references therein.
- (2) Chen, F.; Huang, L.; Li, Q. *Chem. Mater.* **1997**, *9*, 2685; Chen, F.; Song, F.; Li, Q. *Microporous Mesoporous Mater.* **1999**, *29*, 315.
- (3) (a) Lind, A.; Andersson, J.; Karlsson, S.; Ågren, P.; Bussian, P.; Amenitsch, H.; Linden, M.; Langmuir, **2002**, *18*, 1380. (b) Lind, A.; Spliethoff, B.; Lindén, M. In press.
- (4) JEOL 1200EXII TEM equipped with Gatan bioscan CCD camera and Gatan 626 cryo holder.
- (5) (a) Bellare, J. R.; Davis, H. T.; Scriven, L. E.; Talmon, Y. *J. Electron Microsc. Technol.* **1988**, *10*, 87. (b) Adrian, M.; Heggeler-Bordier, B.; Wahli, W.; Stasiak, A. Z.; Stasiak, A.; Dubochet, J. *EMBO* **1990**, *9*, 4551.
- (6) Regev, O. *Langmuir* **1996**, *12*, 4940.
- (7) Danino, D.; Talmon, Y.; Levy, H.; Beinert, G.; Zana, R. *Science* **1995**, *269*, 1420.
- (8) Yaacob, I. Y.; Bose, A. *J. Colloid Interface Sci.* **1996**, *178*, 638.
- (9) Regev, O.; Guillemet, F. *Langmuir* **1999**, *15*, 4357.
- (10) Marques, E. F.; Regev, O.; Khan, A.; da Graca Miguel, M.; Lindman, B. *J. Phys. Chem. B* **1998**, *102*, 6746.

JA0289301