Coaxial cylindrical bilayer growth: a novel phase in inorganic–surfactant systems evidenced by transmission electron microscopy

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A novel aluminophosphate ($AlPO_4$)-surfactant mesophase is shown to be present by transmission electron microscopy (TEM); it consists of coaxial cylindrical surfactant/inorganic bilayers with an overall diameter of *ca.* 150 nm self aggregated into a hexagonal-like array.

Since the discovery of the M41S silica-based crystalline mesoporous molecular sieves and their preparation in the presence of surfactants,[1,2] these materials have attracted increasing attention, because of their potential applications as catalysts and as advanced materials. Their formation involves cooperative organization of organic and inorganic species;[3–6] the mechanism includes the formation of inorganic–organic ion pairs followed by their self organization into a mesophase and the condensation of the inorganic species into a rigid structure. The active participation of the inorganic species is a key factor in governing the morphology of the organic–inorganic mesophase.[3–6] In addition to in-depth analysis of mechanistic pathways, this field has undergone two major developments, (*i*) the extension of the same synthesis strategy to a large number of oxides,[5–7] and (*ii*) the synthesis of mesoporous metallosilicates.[8–12] In the preceding paper, Sayari *et al.*[13] used long-chain alkylamines to prepare a series of lamellar aluminophosphates ($AlPO_4$) with *d*-spacings in the nanometer range. They found that as most inorganic species except silicates, aluminophosphates exhibit a strong tendency towards the formation of lamellar mesostructures. However, under the synthesis conditions used here, the lamellar $AlPO_4$–$C_{12}H_{25}NH_2$ phase seems to coexist with a novel mesostructure consisting of coaxial cylindrical bilayers stacked in a hexagonal array. This packing, reminiscent of biological structures like liposomes has no equivalent among surfactant liquid-crystal phases. Here we report TEM evidence for the existence of this novel mesophase.

An $AlPO_4$–$C_{12}H_{25}NH_2$ sample was prepared hydrothermally using a gel with the molar composition $P_2O_5:Al_2O_3:C_{12}H_{25}NH_2:60\ H_2O$. Preparation details were reported elsewhere.[13] The presence of only 00*l* reflections in the X-ray powder diffraction (XRPD) pattern was interpreted as arising from a lamellar phase. The interlayer distance determined by the Bragg angle of the most intense peak was 3.11 nm. Solid-state NMR spectroscopy revealed that the connectivities of Al and P are consistent with the formation of $AlPO_4$ layers.[13]

Chemical composition of individual particles determined by EDAX showed that within experimental error, the P : Al ratio was 1 : 1 throughout the sample. However, TEM showed that despite the chemical homogeneity of the inorganic framework, the particles were structurally different, indicating that the material was not a single mesophase. The electron micrograph in Fig. 1 shows a series of parallel and straight fringes. The corresponding electron diffraction (ED) pattern consists of a single row of spots, indicating a lamellar surfactant–inorganic mesophase, as suggested by XRPD. The electron micrograph in Fig. 2(*a*) shows a disk displaying alternating concentric dark and bright rings. The disks had similar overall diameters of *ca.* 130–150 nm, and aggregated into a hexagonal-like array, forming a novel type of mesophase as shown in Fig. 2(*b*). The dark areas in the array are the disks, and a close-up is shown in Fig. 2(*c*). The distance between consecutive rings is equal within experimental error to the interlayer distance in the lamellar phase, 3.05 and 3.07 nm respectively, indicating that both phases are interrelated.

Measurement of successive diameters on different disks showed identical ring structures. This points to growth around a central nucleus, always the same, rather than an inward and outward growth starting from the accidental closure of a bilayer to form an initial ring, which would give different sets of diameters on different disks. The diameter of this central tubule is about 3.6 nm, pointing to a central rod like surfactant micelle encapsulated in the inorganic material. This kind of growth could be rationalized with a system mostly favourable to the formation of lamellae, but also with a slight tendency to form rod like micelles, playing the role of nuclei for further cylindrical growth under the effect of surface forces. By surface forces, these nuclei drive the subsequent formation of closed coaxial bilayers. As shown in Fig. 3, the observed alternating concentric dark and bright rings are interpreted as the edge projections of cylindrical layers of inorganic $AlPO_4$ materials separated by cylindrical vesicles of surfactant, wrapped around a single rod like micelle. Owing to the similar interlayer spacing, the lamellar mesophase may be quite difficult to distinguish from the coaxial cylindrical phase by XRPD.

Both phenomena, of concentric growth of rings to form large disks with similar diameters, and aggregation of these disks into a fairly ordered phase, are quite striking. This amazing structure has some similarities with the vesicular structures encountered

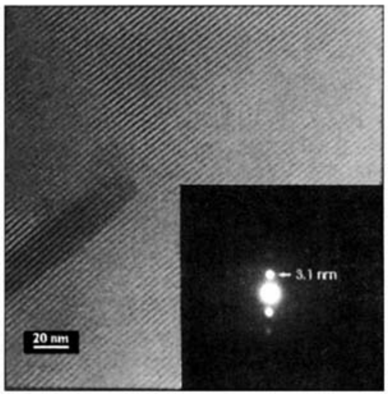

Fig. 1 TEM image of particles showing straight fringes, (interfringe distance ≈ 3.05 nm) with its corresponding selected area ED pattern (d_{100} ≈ 3.10 nm). Image and diffraction pattern are rotated with respect to one another by magnetic lenses. TEM and ED were performed on a Philips CM20 electron microscope, operated at 200 kV. Chemical analysis of individual particles was performed in the microscope, with an EDX spectrometer (Link Oxford Company). Images were recorded with a sensitive CCD camera (Gatan). Samples were dispersed ultrasonically in ethanol, and a drop of the suspension was deposited on a holey carbon grid.

for certain systems involving aqueous solutions of phospholipids[14,15] or zwitterionic alkyldimethylaminoxides.[16] In contrast, the formation of vesicles from surfactants with a small head group such as a single-chain alkylamine is theoretically unexpected. Cylindrical vesicles are even less likely to appear because they are thermodynamically less stable than flat bilayers.[17] However, it is clearly demonstrated that under our synthesis conditions, the addition of inorganic ($AlPO_4$) precursors to a single-chain alkylamine, leads to the formation of vesicle-like structure. This indicates the strong influence of inorganic species on the phase behaviour.[5] Note that Huo *et al.*[18] also synthesized recently a silicate mesophase with a three-dimensional hexagonal symmetry which has no liquid-crystal mesophase counterpart.

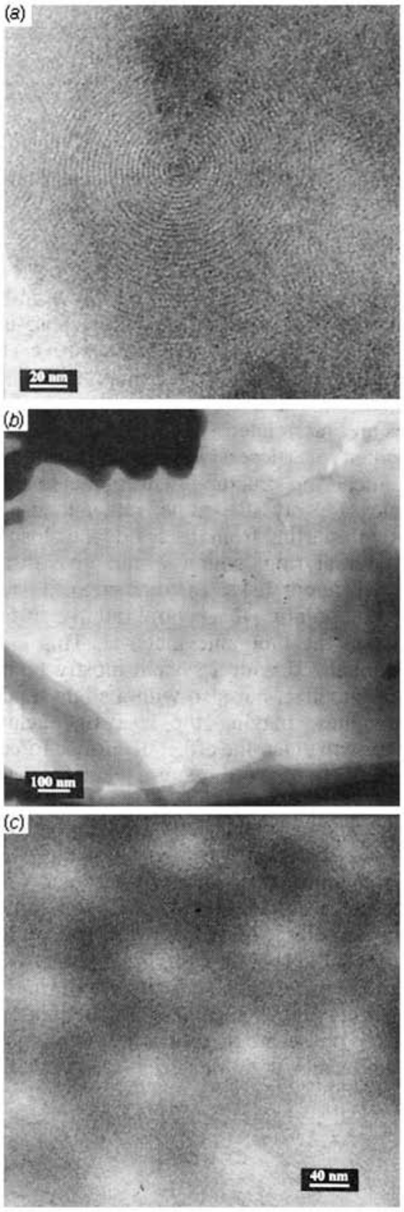

Fig. 2 (*a*) TEM image showing concentric rings, the distance between consecutive rings is *ca.* 3.07 nm; (*b*) TEM image showing a hexagonal-like array of disks; (*c*) close-up showing array of concentric rings

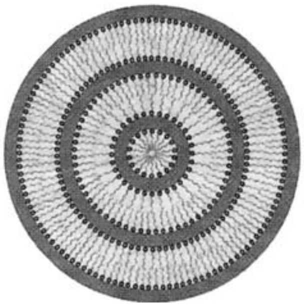

Fig. 3 Schematic illustration of the inorganic–organic bilayers coaxially wrapped around a rod like micelle and viewed down the axis

A transformation from a pre-existing lamellar phase to cylindrical bilayers cannot be considered, because the spontaneous curvature of sheets under isotropic conditions requires an intrinsic structural asymmetry which is absent from the lamellar phase. In addition, the identical sets of diameters observed for different disks point to a growth from a nucleus. In the interpretation developed above, the curvature of bilayers around the rod like nucleus stems from surface forces.

In conclusion, the characterization of individual particles as small as 400 Å, by electron microscopy and diffraction has proved to be a powerful way to evidence a novel mesophase of coaxial cylindrical bilayers in the $AlPO_4$–dodecylamine system. This remarkable structure, which seems to originate from a lamellar growth around a micellar rod like nucleus, has no equivalent among inorganic–surfactant systems or lyotropic surfactant liquid-crystal phases.

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