

Phase behavior of surfactant-inorganic oxides liquid crystals

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The synthesis of surfactant-templated nanostructured materials has attracted the attention of the scientific community because it provides the possibility of tailoring pore size, geometry and surface chemistry through control of the synthesis conditions. Potential applications of these materials range from separations and catalysis to the production of biomimetic materials and devices for optical and electronic applications. Several synthesis protocols have been developed in the last ten years and are the focus of recent reviews¹⁻². Different protocols involve a variety of surfactants -cationic, anionic, nonionic and block copolymers- and a wide range of synthetic conditions including acid or alkaline synthesis, as well as high and low surfactant concentration in the initial surfactant solution.

Despite the extensive experimental effort to control the structure and composition of templated nanoporous materials, molecular modeling of the different processes has remained elusive. The description of such systems is complex due to the overlapping of kinetic and thermodynamic effects.

In this work we are interested in describing the bulk synthesis of surfactant templated silica materials, based on experimental evidence that surfactant-silica liquid crystal phases can be obtained under no silica polymerization conditions, where true lyotropic liquid crystal phases (hexagonal or lamellar) are in equilibrium with a solvent rich phase that may contain a small amount of free surfactant and silica species³. These mesophases are prepared under highly alkaline conditions, from separate isotopic aqueous inorganic and surfactant precursors containing multiply charged anionic silicate oligomers and cationic micelles, respectively. We have shown that the formation of liquid crystal phases containing a high concentration of surfactant and inorganic oxide can be described by a simple lattice model⁴. In this model, strong attraction between the surfactant and the inorganic oxide leads to the formation of liquid crystal phases despite the fact that many important factors, such as hydrogen-bond type interactions, the presence of cosolvents and detailed composition of the solutions are not considered. We model neutral surfactants under the as-

sumption that this behavior is not specific to ionic surfactants, but results from the absence of appreciable inorganic polymerization.

Surfactants are modeled as chains of connected hydrophobic and hydrophilic beads on a lattice and thermodynamic properties are calculated using Monte Carlo simulations in the canonical ensemble. The results presented here are for a symmetric surfactant H_4T_4 , where the surfactant head segments, H , are the hydrophilic and the surfactant tail segments, T , are hydrophobic. These models of surfactants are widely used to study surfactant-water-oil systems, where the surfactant tail segments are oil-like and the surfactant head segments are water like. In this work, the solvent and the inorganic component occupy single sites in the lattice.

In the systems studied, the solvent and the inorganic oxide have favorable interactions with the surfactant head, but the inorganic oxide-surfactant interactions are stronger than the solvent-surfactant interactions, which leads to a phase separation, regardless of the oxide-solvent miscibility. The formation of ordered liquid crystal phases is observed in the phase containing a high surfactant concentration, and the structure of this phase depends on the system composition and strength of the interactions.

The formation of hexagonal and lamellar structures at different conditions is in qualitative agreement with experimental evidence on the formation of surfactant-silica liquid crystals and the synthesis of MCM-41 type materials. We also show that the increase in surfactant solubility in the solvent-rich phase with temperature can result in a lamellar to hexagonal transformation.

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