

The interaction between the surfactant and the co-structure directing agent in anionic surfactant-templated mesoporous silicas

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ABSTRACT

Anionic surfactant-templated mesoporous silicas (AMS) are synthesized with a co-structure directing agent (CSDA) that interacts with both the organic and inorganic components of the system. The AMS materials structure is controlled by pH. We investigated the formation of AMS cubic and hexagonal phases, prepared under the same conditions, except pH, by EPR spectroscopic measurements. We used silica-like and surfactant-like spin probes added to the reaction mixtures in minute amounts. Through the spin probes we resolved the specific interactions of the CSDA (*N*-trimethoxysilylpropyl-*N,N,N*-trimethyl ammonium chloride (TMAPS)) with the surfactant (sodium myristate (C14AS)) and the polymerizing silica. We observed for both phases a fast formation of a mesophase upon addition of the silica precursor (TEOS, tetraethoxysilane) and the CSDA into the surfactant solution, attributed to the strong attraction between the CSDA and the anionic surfactant. This is then followed by a slow condensation of the silica. Electron spin echo envelope modulation (ESEEM) spectra of both spin probes in the as-synthesized materials indicated the presence of two types of CSDA molecules; one interacting with the surfactant and the other with the silica wall. Continuous wave EPR spectra showed different spin probe motilities in the two as-synthesized materials that indicated that the relative populations of the two CSDA types are different in the two phases. We attribute this difference to the pH differences in the reaction mixtures. A soft extraction of the surfactant from the pores did not alter the structure of the final materials, but it abolished the observed molecular level differences between them. The extraction allowed the pending ammonium groups to acquire a high degree of freedom and accessibility to water molecules.

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1. Introduction

Synthesis of ordered mesoporous silicas relies on the self-assembly of a surfactant template and inorganic silica precursors into a mesostructure [1,2]. This self-assembly depends on the intimate interactions between the surfactant and the inorganic oxide source. Accordingly, different synthesis routes were classified according to the type of the interaction: S^+I^- , S^-I^+ , $S^+X^-I^+$, $S^-X^+I^-$, S^0I^0 , $S^0H^+X^-I^+$, and so on, where S, I and X represent the surfactant, the inorganic (silica) precursors, and a counter ion, respectively, with their charge depending on whether they are in a cationic, anionic or neutral form [3,4].

The synthesis of ordered mesoporous materials is based on a sol-gel process, in acidic or basic environment [5]. Therefore, the choice of surfactant and reaction conditions determine the interactions driving the mesostructure formation. For example, in the case of silica materials the pH is crucial, considering that the isoelectric

point of silicates species is around 2 [6]. Cationic and neutral non-ionic surfactants have been proven very successful in forming diverse mesostructures, in acidic or basic conditions [1,7–10]. However, anionic surfactants have not yielded ordered mesostructure silicas unless a co-structure directing agent (CSDA) was added to the synthesis [11]. This CSDA has an alkoxysilane on one end that can co-condense with the silica precursor, and an ammonium group on the other end that can interact with the negatively charged head group of the surfactant, actually acting as glue. Using this strategy, a variety of structures, including cubic, tetragonal, hexagonal, bicontinuous cubic, and lamellar, as well as chiral structures, were successfully prepared [11–16].

The different mesostructures obtained were explained to some extent by the packing parameter of the surfactant $g = v/a_0l$, where v is the chain volume of the surfactant, a_0 is the effective hydrophobic/hydrophilic interfacial area and l is the kinetic surfactant chain length [17,18]. This parameter depends on the structure of the components of the system and predict the curvature of the aggregate, and therefore the final mesostructure. The g parameter has been shown to be sensitive to the surfactant concentration, temperature and the presence of other species in the solution [19,20].

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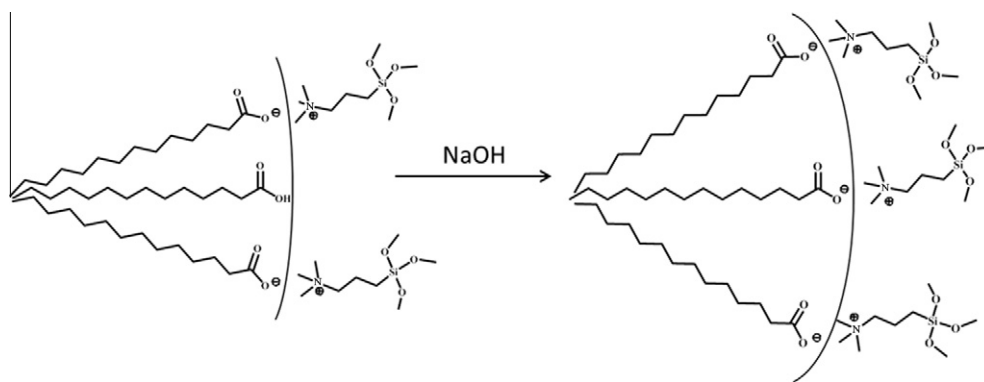


Fig. 1. A schematic representation of the change of curvature of the surfactant micelles by modifying the ionization degree of the anionic surfactant through a change of pH. The positively charged CSDA is shown as well.

It has been proposed that the packing parameter of the anionic surfactant can be controlled through the degree of ionization of the surfactant, which depends on the pH, as shown on Fig. 1. The degree of ionization of the polar head of the carboxylic fatty acids increases with pH, thereby increasing its effective headgroup area due to repulsion and leading to a lower g value. Indeed, by increasing the pH of the reaction mixture a transition from lamellar to cylindrical and to cage-type mesophases was observed. This, in turn, was correlated with an increase of curvature due to the decrease of g [14]. Other parameters reported to affect the structure of the anionic surfactant-templated silicas are the time delay between the addition of CSDA and the silica source [16], the structures of the CSDA and of the surfactant [13], and the molecular CSDA/surfactant ratio [15].

In addition to the possibility to control the structure of the final phase, the anionic pathway received attention also for its ability to easily provide functionalized mesoporous silicas. The possible removal of the surfactant by extraction, instead of calcination, allows retaining the amino or ammonium group of the CSDA in the pore as it is bound to the silica walls [21]. ^{13}C NMR and elemental analysis of the functionalized material thus obtained showed a homogeneous distribution of amine or ammonium groups. Their loading amount was reported to be limited by the quantity of CSDA that can interact electrostatically with the anionic surfactant [21].

A previous study on the synthesis of AMS, using the acid form of a surfactant and a CSDA with an amino group, showed that the reaction takes different paths, depending on the time between the addition of CSDA and the addition of the silica source, yielding different phases. Following its addition into the solution, the CSDA was reported to quickly interact with the surfactant and to start condensing. An organo-silica layer made of condensed CSDA was shown to first form around the micelles in solution. The inorganic silica species condense later to form an outer inorganic silica shell. As the reaction goes on, the system just shows an increase of the fraction of condensed inorganic silica [22].

Herein we used spin probe EPR methods to explore the interplay between the surfactant, CSDA and the silica in hexagonal ($p6mm$) and cubic ($Fd\bar{3}m$) structures. We used a surfactant in its salt form, sodium myristate (C14AS), and a CSDA with a quaternary

ammonium group, *N*-trimethoxysilylpropyl-*N,N,N*-trimethyl ammonium chloride (TMAPS). In this combination, the ionization degree of the CSDA is not modified by pH while that of the surfactant is. C14AS is a common surfactant whose phase diagram in water is well known [23]. Its 1% wt Krafft point has been determined around 44 °C, above which it dissolves in water to form a clear micellar solution [24]. It is known that at equilibrium a dilute aqueous solution of sodium myristate ($C < 20$ mM, corresponding to $\text{pH} < 10$) have a protonation fraction of about 1%, but this has a strong influence on the solution and phase behavior [25]. By adding NaOH the protonation can be further decreased, but the solubility of C14AS decreases as well. The addition of other electrolytes, and especially tetraalkylammonium salt affects also significantly the solution behavior of C14AS [24].

Spin probe EPR has been proven successful to characterize pores and surface properties [26–30]. The formation of mesoporous silica materials, synthesized with cationic or neutral surfactant templates, has also been monitored using in situ continuous wave (CW)-EPR [31–36], and more advanced pulse EPR experiments, such as electron spin echo envelope modulation (ESEEM) [37–39]. In general, surfactant-like nitroxides, were used to probe local changes in the organic phase, and a nitroxide linked to an alkoxy-silane was employed to give information on the formation of the silica wall [40]. The CW-EPR spectrum of the spin probes provide information on the dynamics and polarity of the microenvironment of the nitroxide label, while ESEEM experiments give information on its local structure via the hyperfine interaction with nearby magnetic nuclei [41,42].

To investigate the formation mechanism and inner surface properties of as-synthesized cubic ($Fd\bar{3}m$) and 2D-hexagonal ($p6mm$) materials, with emphasis on the CSDA interactions with the other components of the reaction, we used 5-doxyl stearic acid (5-DSA) as a surfactant-like probe, and a silica-like probe, 2,2,6,6-tetramethyl-4-[3-(triethoxysilyl)propylamino]-1-piperidinoxy (SL1SiEt) that can co-condense with the silica precursor (see Fig. 2). Whatever the phase, we observed that the addition of the silica mixture (CSDA + silica precursor, (TEOS, tetraethoxysilane)) leads to a fast (2–8 min) formation of a mesophase, whose exact kinetics is below our experimental resolution. We could only observe the

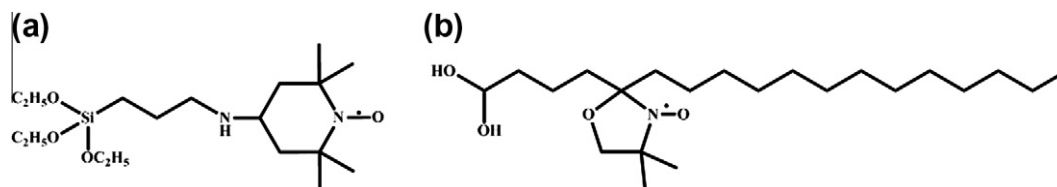


Fig. 2. (a) The nitroxide radical, SL1SiEt, used to probe the silica region and (b) the 5-DSA employed for probing the surfactant part of the system.

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