

Self-Assembly of Silicate-Surfactant Liquid Crystals During Mesophase Materials Synthesis

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Introduction

The discovery of silicate mesoporous molecular sieves by Mobil researchers (1) has prompted new general strategies for the synthesis of periodic inorganic arrays. This new synthesis methodology is based on cooperative self-assembly of inorganic and surfactant species, driven predominantly by interfacial interactions, such as charge density, and geometric constraints among the inorganic species and *aggregates* of organic surfactant molecules (2, 3). Such an approach is related to tactics employed in the synthesis of microporous molecular sieves, in which the interactions, and thus nucleation and growth, occur among inorganic species and *single* organic molecules. Recently, considerable effort has been directed toward chemical synthesis, structural characterization, and understanding the assembly mechanism of inorganic-surfactant mesophases (1-8), which are intermediates to the formation of inorganic mesoporous molecular sieves.

Establishing the underlying mechanism by which these materials form is crucial to the design and control of macroscopic mesophase material properties (1-3, 5-8). In particular the presence of highly charged anionic silicate species can be important to the formation of silicate-surfactant mesophases, whose phase behavior is further complicated by the multicomponent nature of typical synthesis mixtures. As we have recently demonstrated, inorganic-surfactant mesophases can be formed with numerous inorganic species, cationic and anionic surfactants, and under various synthesis conditions (5). Furthermore, under certain conditions, the process of mesophase self-assembly may be strongly coupled to time-dependent polymerization kinetics of silicate species at the inorganic-organic interface (2). To separate the effects of silica polymerization

from the thermodynamics of mesophase self-assembly, low temperatures, high pH, and stable anionic silicate species have been used. This ensures that under these conditions, thermodynamic equilibrium can be reached without appreciable silicate polymerization, thus permitting stable formation of silicate-surfactant mesophases, which can be intermediates to subsequent mesoporous structures. We have used this approach to show that in the absence of inorganic polymerization, these mesophases have liquid crystalline properties, similar to those of conventional aqueous lyotropic liquid crystal (LLC) systems (2). Here, we describe the process by which phase separation of the silicate-surfactant liquid crystals occur by considering the relevant interactions contributing to the total Gibbs free energy of the system. It will be shown that silicate-surfactant liquid crystal formation can be induced through manipulation of the inter-aggregate forces among organic micelles by adding a highly basic inorganic solution containing multiply charged anionic silicate species.

No pre-existing long-range order is necessary to form silicate-surfactant liquid crystals, which can be synthesized beginning with isotropic surfactant and silicate precursor solutions (2). Depending on the concentration of a dilute cationic surfactant solution, for example 0.03-20 wt% cetyltrimethylammonium bromide (CTAB) at room temperature, the organic precursor solution consists of spherical or cylindrical micelles in equilibrium with single surfactant molecules (9). With the CTAB molecules deuterated at the α -carbon position, a single narrow peak is observed in the ^2H nuclear magnetic resonance (NMR) spectrum of such a precursor solution (Fig. 1A), reflecting its isotropic character and the absence of long-range order prior to addition of the silicate species. At pH 12.5, the inorganic precursor solution consists of a distribution of silicate anions (10), which at room temperature, have been shown by ^{29}Si NMR to be mainly in the form of double-four-ring (D4R) oligomers, $[\text{H}_n\text{Si}_8\text{O}_{20}]^{(8-n)-}$ (2, 11).

Combining the inorganic and organic precursor solutions results in the formation of a two-phase system: (i) a lyotropic silicate-surfactant liquid crystalline phase with high concentrations of silicate and surfactant species, and (ii) an aqueous-rich phase with low silicate and surfactant concentrations. The surfactant molecules in each phase contribute to the ^2H NMR spectrum of the two-phase system. Consequently in Figure 1B, the axially symmetric Pake pattern with a quadrupolar splitting of 12.6 kHz corresponds to the surfactant molecules confined within the anisotropic geometry of a particular aggregate, in

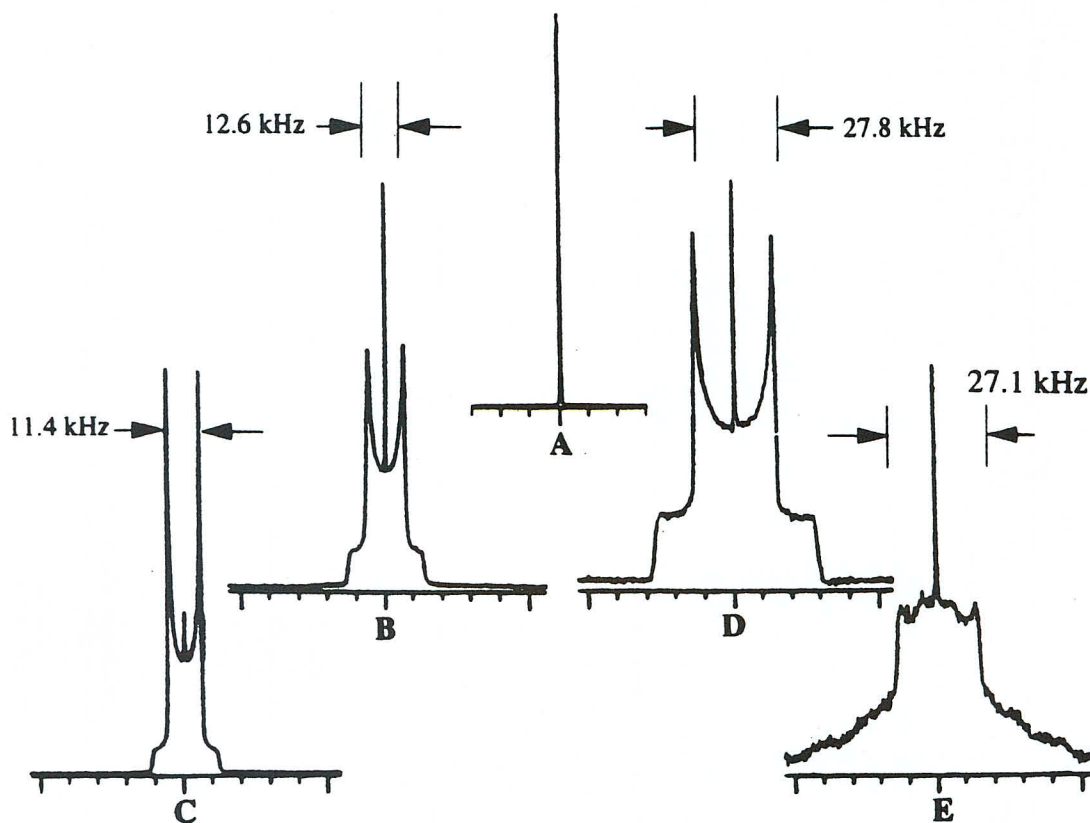


Figure 1. ^2H NMR spectra of α -deuterated CTAB in (A) a 6.8 wt% aqueous micellar solution at 25°C ; (B) a hexagonal silicate-surfactant mesophase at 25°C with a molar composition of 1.4 SiO_2 , 196 H_2O , 0.5 $(\text{TMA})_2\text{O}$, 0.25 $(\text{C}_{16}\text{TMA})_2\text{O}$, 18.8 CH_3OH ; (C) a 30 wt% aqueous micellar solution at 35°C in a hexagonal LLC phase; (D) a lamellar silicate-surfactant mesophase at 25°C with a molar composition of 1.4 SiO_2 , 196 H_2O , 0.5 $(\text{TMA})_2\text{O}$, 0.25 $(\text{C}_{16}\text{TMA})_2\text{O}$, 18.8 CH_3OH , 1.2 TMB; (E) a mesophase obtained from (D) at 10°C corresponding to the onset of chain freezing. The base and organic solute used were tetramethylammonium hydroxide (TMAOH) and trimethylbenzene (TMB), respectively. All spectra were acquired with a ^2H $\pi/2$ pulse of typically 4–6 μs , a 50- μs echo delay, and a repetition delay of 0.25 s.

this case a rod-like structure in a hexagonal silicate-surfactant mesophase (i), while the narrow isotropic feature corresponds to the randomly mobile surfactant species (e.g., micelles) in the aqueous phase (ii) (2). A micelle is an aggregate structure in which surfactant molecules have a short (10^{-4} s) residence time. For surfactant species in aggregates in concentrated liquid crystalline phases,

molecular residence times are many orders of magnitude longer (up to 10^{+4} s) (12).

Thermodynamics of Surfactant Self-Assembly

The self-assembly of inorganic-organic mesophases can be understood by examining the various contributions to the Gibbs free energy of the multicomponent system (12). At a given composition and temperature, the structure with the lowest free energy will of course be the thermodynamically preferred morphology. The total Gibbs free energy can be written as the sum of enthalpic contributions associated with forces within (H_{intra}) and among (H_{inter}) individual aggregates, plus entropy of mixing effects S which are a function of the volume fraction of the aggregates in the mixture (13):

$$G_{total} = [H_{intra} + H_{inter}] - TS$$

The term H_{intra} corresponds to interactions within a particular aggregate, and accordingly can be written as the sum of various electrostatic, hydrophobic, steric, and chain packing contributions:

$$H_{intra} = H_{es,intra} + H_{hydrophobic} + H_{steric,intra} + H_{chain}$$

For example, $H_{es,intra}$ is a repulsive contribution arising from the electrostatic forces associated with charged surfactant and counter-ion species. This term increases the mean area-per-head-group, a_o , available to each surfactant head group in an aggregate. The attractive hydrophobic term, $H_{hydrophobic}$, arises from effects that lower the interfacial contact area between the surfactant alkyl chains and the water, thereby reducing a_o . $H_{steric,intra}$ accounts for steric repulsions among adjacent surfactant head groups and is an excluded volume effect, while H_{chain} represents packing and accompanying conformational features of the surfactant chains. The intra-aggregate enthalpic terms in H_{intra} , along with molecular geometrical considerations, can be used in molecular packing models to predict the particular structure of an aggregate (14). The aggregate geometry is also predictable using a mean-field continuum approach, in which the intra-aggregate energetic terms are implicitly contained in an aggregate bending energy, which is characterized by the elastic modulus of curvature, K (15).

At low surfactant concentrations the inter-aggregate interactions described by H_{inter} are weak, so that the intra-aggregate contributions to the Gibbs free energy are the only relevant terms. At higher surfactant

concentrations depending on the counter-ion, however, H_{inter} is important and can similarly be written as a sum of contributing effects:

$$H_{inter} = H_{es,inter} + H_{steric,inter} + H_{vdW}$$

$H_{es,inter}$ accounts for the long-range double-layer electrostatic repulsions among adjacent aggregates, and in simple cases (e.g., in the presence of monovalent counter-ions), can be quantitatively treated using the Poisson-Boltzmann equation (16). The effective range of this interaction depends on solution conditions, as it decreases with increasing ionic strength (e.g., in the presence of high electrolyte concentrations or multivalent ions). The magnitude of $H_{es,inter}$ at small aggregate separations is, however, enhanced at higher ionic strengths (12). Furthermore, for systems with divalent ions, correlated fluctuations in the spatial ionic charge distribution of two adjacent aggregates have been shown, theoretically (17) and experimentally (18), to produce an attractive van der Waals-type interaction. The repulsive steric term, $H_{steric,inter}$, is due to thermal fluctuation modes (e.g., undulation and protrusion), and it tends to maximize the inter-aggregate separation. H_{vdW} is an attractive contribution that accounts for the long-range electrodynamic van der Waals forces among different aggregates. In addition, in these concentrated systems, translational entropy of mixing effects in S are small, so that entropy differences between dense anisotropic liquid crystalline phases can generally be neglected. Here, the entropy loss arising from confinement of two adjacent aggregates within a space is accounted for by $H_{steric,inter}$ (19).

Generally the solution conditions, such as ionic strength, pH, temperature, and composition, influence H_{intra} and H_{inter} in a highly interdependent fashion. For example, for negatively charged lipid bilayers it has been established that the addition of divalent cations and/or the reduction of pH reduces the mean head-group-area a_o of the surfactant species by screening the intra-aggregate electrostatic repulsions (20). Furthermore, inter-bilayer repulsions are also more effectively screened, which reduces layer separation in multilayer phases and accounts for increased adhesion or fusion of vesicles (21).

Silicate-Surfactant Liquid Crystalline Mesophases

^2H and ^{13}C NMR measurements can be utilized to obtain insight on liquid crystalline systems and can specifically be used to probe the phase behavior and surfactant chain dynamics of the silicate-surfactant mesophases. The 12.6 kHz quadrupolar splitting in the ^2H NMR spectrum of the hexagonal

silicate-surfactant mesophase obtained at room temperature (Fig. 1B) is comparable to a typical hexagonal LLC splitting of 11.4 kHz at 35°C (Fig. 1C) (2). This indicates that the anisotropic time-averaging of the quadrupolar interaction is very similar in the silicate-surfactant and binary LLC systems. Similarly for a D4R silicate-cetyltrimethylammonium-trimethylbenzene mixture, the 27.8 kHz quadrupolar splitting in Figure 1D has been assigned to planar aggregates belonging to a lamellar silicate-surfactant mesophase. Using geometric arguments, and assuming an equivalent order parameter at a given temperature, one can show that the ^2H quadrupolar splitting for deuterated surfactant species undergoing lateral motion in a lamellar phase should be twice that for such species moving rapidly within the cylindrical aggregates of a hexagonal phase (22). The observed splittings (lamellar 27.8 kHz, hexagonal 12.6 kHz) indicate residual excess splitting for the lamellar phase that is above the expected factor of two, pointing to a larger local order parameter for the α -carbon group in the aliphatic chain of the lamellar silicate-surfactant mesophase (11).

Self-assembly of silicate-surfactant aggregates as described above, produces a colloidal *liquid crystalline* mesophase that is entirely distinct from the *crystalline* precipitates which form below the Krafft temperature of a surfactant mixture. The concentration-dependent Krafft temperature, T_c , is formally defined as the temperature below which micelles are insoluble (23) and is closely related to the H_{chain} component of the intra-aggregate interactions. Generally, as T_c is approached from above, the flexible aliphatic surfactant chains become rigid, with the result that the surfactant molecules can no longer pack into curved micellar structures. Under these circumstances, the micelles become unstable and *crystalline* aggregates precipitate out of the solution (23). This, however, is in contrast to the clear evidence in Figures 1B and 1D of the *liquid crystalline* properties of the D4R silicate-cetyltrimethylammonium colloidal mesophases. Moreover, reducing the temperature of the lamellar silicate-surfactant mesophase shows that this system has a Krafft temperature T_c of approximately 10°C, as evident from the broadening and loss of axial symmetry of the ^2H line shape in Figure 1E due to the onset of chain freezing. The reduction of the Krafft temperature caused by ion-exchange of the Br^- counter-ions with the larger D4R oligomers (described below) is consistent with results from other surfactant mixtures, where T_c is depressed with increasing counter-ion size in otherwise identical systems (24).

Corroborative investigation of surfactant chain dynamics is provided by ^{13}C NMR cross-polarization studies, which are sensitive to molecular motions with characteristic frequencies on the order of tens of kilohertz. Figure 2 reflects the surfactant chain dynamics of three closely related cetyltrimethylammonium surfactant systems: a hexagonal binary LLC phase at 35°C , a hexagonal silicate-surfactant mesophase at 25°C , and monoclinic crystalline CTAB. Due to the highly dynamic characteristics of the surfactant molecules in the two liquid crystalline phases, the proton spin-lattice relaxation time in the rotating frame of reference, $T_{1\rho\text{H}}$, is long. As a result, the ^{13}C NMR signal intensity produced by cross-polarization from dipole-dipole coupled protons increases monotonically up to ^1H - ^{13}C contact times of approximately 15 ms for carbon atoms in the aliphatic chains. This is in sharp contrast to measurements made on crystalline CTAB, where more rapid proton $T_{1\rho\text{H}}$ relaxation results in diminished aliphatic ^{13}C NMR signal intensity after a short buildup period. The superposition of the ^{13}C intensity curves for the hexagonal LLC and silicate-surfactant mesophases in

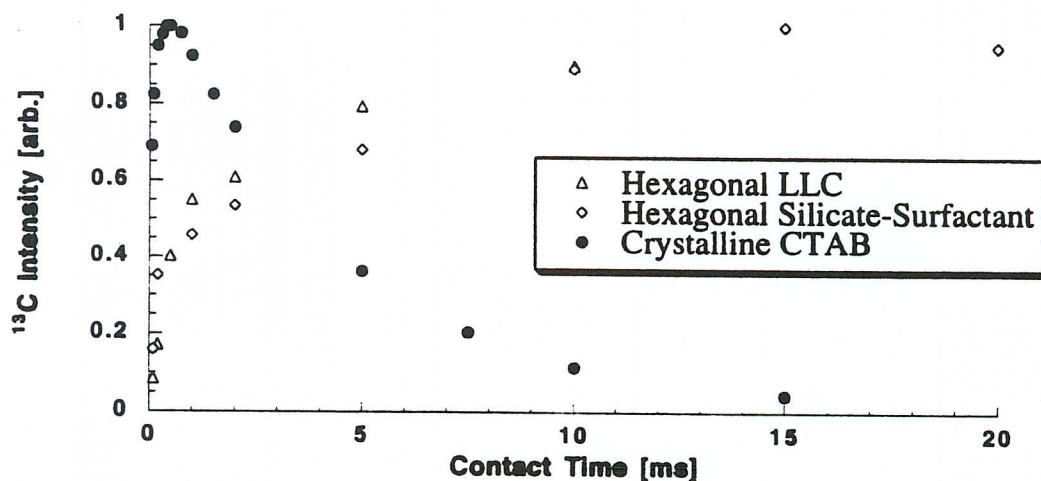


Figure 2. ^{13}C NMR signal intensity measured for carbon atoms in the cetyltrimethylammonium aliphatic chains of different surfactant systems as a function of cross-polarization (CP) contact time with dipole-dipole coupled proton spins. Mobility of the surfactant molecules increases the $T_{1\rho\text{H}}$ relaxation time of the proton spins, which influences the cross-polarization efficiencies reflected by the curves: a hexagonal binary LLC phase at 35°C (Δ), a hexagonal silicate-surfactant mesophase at 25°C (\diamond), and monoclinic crystalline CTAB (\bullet). All CP data were obtained under conditions of magic-angle spinning (CP/MAS) with sample rotation rates of 3 or 4 kHz, for the two liquid crystalline or solid crystal samples, respectively.

Figure 2 confirms that the silicate-surfactant system is above its Krafft temperature T_c , consistent with its liquid crystalline properties (Figs. 1B, 1D). These results are corroborated by recent polarized optical microscopy and small-angle X-ray diffraction measurements (11).

Self-assembly of a silicate-surfactant mesophase is governed by the inter-aggregate contribution H_{inter} to the total Gibbs free energy. Generally, depending on the magnitude of the various terms in H_{inter} , two general scenarios could transpire (12). The first occurs when the repulsive terms dominate the attractive ones, for example in the absence of added electrolyte or salt (i.e., in the so-called weak-screening limit), where $H_{es,inter}$ is the most relevant term. Here, with increasing surfactant concentration, the surfactant molecules rearrange into an ordered array of aggregates, so that the inter-aggregate spacing is maximized. This is the case for the LLC phases of the binary CTAB/water system, where with increasing surfactant concentration the natural progression of phases is hexagonal, cubic, and lamellar (9). Furthermore, because the aggregates minimize the Gibbs free energy of the system by repelling one another, a typical LLC fills the entire volume of a one-phase solution (12).

Alternatively, for cases where the attractive forces dominate the repulsive interactions, the aggregates can coalesce and phase separate to produce two coexisting phases within the sample: (i) a liquid crystalline phase and (ii) an aqueous-rich phase containing soluble micelles and/or monomers (12). This behavior is characteristic of the silicate-surfactant liquid crystal self-assembly process. Addition of multiply charged anionic silicate (e.g., D4R) oligomers in highly basic solution to a dilute aqueous surfactant mixture lowers the surface potential or charge of a given cationic micelle by enhancing the ionic association constant and by increasing the pH. This leads subsequently to more effective screening of the inter-aggregate double-layer repulsion, as represented by $H_{es,inter}$. Such analysis is based on separate *in situ* ^{29}Si NMR studies of silicate-surfactant mesophase self-assembly, which indicate that the multiply charged D4R anions compete with and ion-exchange for the monovalent Br^- counter-ions (2, 11). This process apparently occurs because of the higher charge density of a D4R anion with respect to a Br^- counter-ion at high pH. Also present are attractive van der Waals-type ion-correlation forces (18, 19) among the D4R anions, which are highly polarizable and mobile in the diffuse double layer surrounding a given aggregate. In addition, the bulky D4R units are expected to reduce $H_{steric,inter}$ associated with the inter-aggregate steric

repulsions. This hypothesis can be rationalized as follows: bulky anionic D4R units strongly associate to the cationic surface of a transient aggregate in a multidentate fashion, which can lead to an increase of the aggregate elastic modulus of curvature, K . Since the repulsive undulation forces caused by collective thermal fluctuations are inversely proportional to K (12), the enhancement of the elastic modulus of curvature can be expected to further diminish repulsive inter-aggregate interactions by reducing $H_{steric,inter}$.

Compared to the electrostatic and steric contributions, $H_{es,inter}$ and $H_{steric,inter}$, the attractive van der Waals term H_{vdW} is less sensitive to variations in electrolyte and pH conditions, and to a reasonable approximation can be considered constant (12). Changes in solution conditions can reduce the repulsive contributions to an extent that the inter-aggregate attractive terms, namely the van der Waals forces among the surfactant molecules and the van der Waals-type ion-correlation forces among the D4R anions, become dominant, thus causing phase separation to occur. In at least one of the resulting phases, this produces high local concentrations of inorganic and organic species, which are capable of establishing the long-range order observed in the liquid crystalline silicate-surfactant mesophases. Moreover, the rapid phase separation observed during the transient self-assembly process suggests that these silicate-surfactant systems reside at their primary potential energy minimum, for example, as described by DLVO theory (12). The occurrence of phase separation indicates that during the silicate-surfactant self-assembly process, the gain in the enthalpic terms exceeds the entropic loss in the total Gibbs free energy.

Self-assembly of a silicate-surfactant mesophase can, thus, be explained by considering the various interaction terms present in the overall Gibbs free energy of the multicomponent silicate-surfactant system. Specifically, silicate-surfactant phase separation may be induced by manipulation of the inter-aggregate forces through changes in solution conditions following the addition of a highly basic inorganic solution containing multiply charged anionic silicate oligomers to an organic micellar solution. Although a complicated problem, by considering the minimum Gibbs free energy calculated at a given composition and temperature, prediction of mesophase morphology should be feasible. Furthermore, the characteristics of the silicate-surfactant mixture in subsequent stages of mesophase material syntheses, including possible phase transformations and inorganic polymerization, can similarly be accounted for by considering the overall free energy of the system (3), in particular the intra-

aggregate interactions. For example, at moderate temperatures (approximately 60°C) a silicate-surfactant lamellar-to-hexagonal phase transformation can be induced by manipulating the H_{chain} term through expulsion of organic solute molecules (e.g., TMB) from the hydrophobic region of the aggregates (2, 11). At temperatures of approximately 100°C or higher, lower pH conditions (e.g., 11.5), and/or with more reactive silicate species (e.g., tetraethoxysilane), appreciable inorganic polymerization can occur to modify the intra-aggregate electrostatic interaction $H_{es,intra}$ according to charge density matching arguments, inducing a similar lamellar-to-hexagonal phase transformation (3). In summary, the self-assembly mechanism of silicate-surfactant mesophases, and separate silicate polymerization at the interface, can be investigated by considering the various intra- and inter-aggregate interactions present in these multicomponent systems. Such studies are expected to provide a firm and general foundation from which syntheses of inorganic-organic mesophase materials may be designed and controlled.

Acknowledgments

We thank Prof. J.N. Israelachvili for helpful discussions. This work was supported by the NSF Young Investigator Program (B.F.C.), the David and Lucile Packard Foundation (B.F.C.), Shell Research B.V. (B.F.C.), and NSF grant MCB-9202775 (G.D.S.). The experiments were conducted on NMR instrumentation supported in part by the NSF Division of Materials Research under grant DMR-9222527 and through the UCSB Materials Research Laboratory under award DMR-9123048. A.F. gratefully acknowledges the Henkel Foundation and the ACS for a research fellowship in Colloid and Surface Chemistry.

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