

Using High Pressure Phase Stability to Determine the Internal Pressure of Silica/Surfactant Composites

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We examine the pressure and temperature dependences of a nanoscale structural rearrangement in periodic silica/surfactant composites with a goal of understanding how the silica framework modifies the molecular environment of the organic surfactant. Hydrothermal treatment is used to force surfactant-templated silica to undergo a phase transition from a hexagonal phase to a lamellar phase; the experiment is carried out both at 0.001 and at 1 GPa. The transition midpoint shifts to a higher temperature when the composite transforms under elevated pressure. Applying the concepts of surfactant packing and compressibility to this curvature-driven transition leads us to estimate the pressure felt by the composite's organic phase when the composite is subjected to an external pressure of 1 GPa. Our results indicate that this internal pressure is approximately 0.1 GPa, which is significantly smaller than the applied pressure of 1 GPa. The results confirm the idea that the high rigidity of the silica framework provides a protected molecular scale environment within the organic domains of the composite.

Periodic hexagonal silica/surfactant nanostructures such as MCM-41^{1,2} are exciting candidates for lightweight materials that are both stiff and mechanically robust.³ The nanoscale architecture allows the highly ordered cross-linked silica framework to resist significant deformation, even when a large hydrostatic pressure is applied. Composites maintain much of their long-range order to pressures as high as 12 GPa.³ Moreover, any pressure-induced distortions that do occur at pressures as high as 12 GPa appear to be almost completely reversible.³ Although compressibilities may be quite low for these composite materials, some volume compression does occur when pressure is applied and this contraction naturally translates to an internal pressure that compresses the organic domains inside the silica framework. Studies using a rigidochromic Re complex to probe the molecular environment inside the organic domains provide a first look at the behavior inside these channels.⁴ These experiments reveal that surfactant tails do not become rigid until an external pressure of almost 10 GPa is reached, suggesting that the internal pressure felt by the organic domains is significantly lower than the applied pressure. This reduced internal pressure can perhaps be described using the concept of fugacity: the free energy of the surfactant is lower than that predicted by the applied pressure. As a result, an "internal pressure" (or fugacity) is needed to describe the state of the surfactant.

This paper further examines this internal pressure by studying the phase stability of silica/surfactant composites as they are treated in water under both elevated pressure and elevated temperature. A variety of work has established that hexagonal-to-lamellar phase transitions in silica/surfactant composites can be driven by temperature-induced changes in the optimal packing of the surfactant.^{5–8} Specifically, changes in surfactant curvature drive the mesostructural changes.^{9,10} Thus, curvature can be used to model our experimental results and the response of the organic phase while the composite is under high pressure.

We estimate the pressure felt by the surfactants in the pores and confirm the idea that the cross-linked inorganic network supports the majority of the applied load.

Composite materials were synthesized using established methods.^{5,9} Eicosyltrimethylammoniumbromide (C₂₀TAB) surfactants used to template the composites were synthesized from N(CH₃)₃Br and CH₃(CH₂)₁₉Br.¹¹ A composite was produced by mixing a basic solution (10.0 g of water, 1.348 g of 2 m NaOH) containing 0.115 g of surfactant with 0.965 g of tetraethyloxysilicate for 1 h. The product was filtered, washed, and dried at room temperature. Structural changes were monitored using real-time X-ray diffraction (XRD).^{5–7,9} Data were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beamline 10–2 using an X-ray energy of 13 keV. For the high-pressure experiments, a 1:2 mixture (by weight) of composite:water was placed inside a 500 μ m diameter sample cell and compressed to 1 GPa using a Merrill-Bassett-style diamond anvil cell (DAC) equipped with 800 μ m culets.^{12,13} The water both provided an isotropic pressure on the composite and was necessary to facilitate the phase transition process.¹⁴ The DAC was heated externally with a resistive heater. The temperature was increased at a ramp rate of 2 °C/min and measured using a thermocouple attached directly to the diamond anvil. Ruby fluorescence^{12,15–17} was used to determine the pressure in the cell, both at ambient and elevated temperatures.¹⁸ For the low-pressure work, the same 1:2 (composite:water) mixture was heated in a quartz capillary using a feedback controlled hot air stream. A modest gas pressure (\sim 0.001 GPa) was used to keep the water from boiling. The details of this experimental setup have been presented elsewhere.⁵ For all experiments, data were collected using a Roper Scientific 1242 \times 1152 cooled X-ray CCD detector; data acquisition times were 45 s at 1 GPa and 30 s at 0.001 GPa. Peak areas and positions were determined by fitting Voigt functions to the angle integrated diffraction data.

Mesostructural evolution of composites under 0.001 and 1 GPa upon hydrothermal treatment are shown in Figure 1. Both

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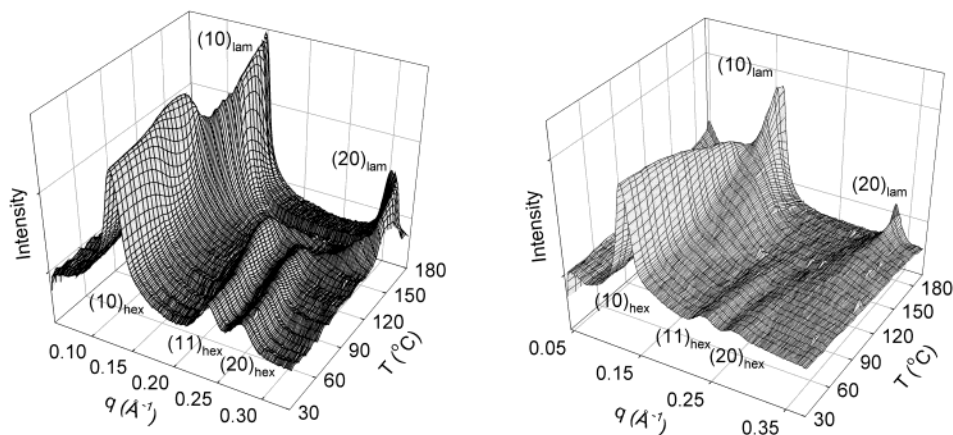


Figure 1. Evolution of mesostructures observed upon heating in water at about 0.001 GPa (left) and 1 GPa (right). A hexagonal-to-lamellar phase transition can be seen in both cases, although the transition temperature is significantly high at 1 GPa. Note that the intensity of the diffraction peaks increase and the relative intensities of the various peaks change upon heating at 0.001 GPa. The changes are associated with the formation of a more regular hexagonal structure. By contrast, peaks show a slow intensity decrease upon heating at 1 GPa, indicating that structural regularization takes place less readily at elevated pressure.

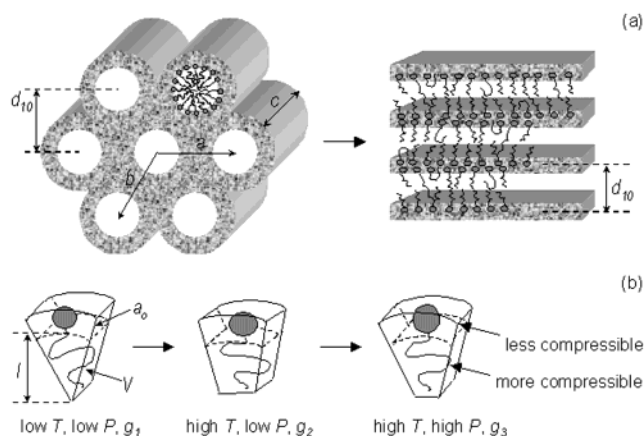


Figure 2. (a) Schematic depicting structural rearrangement from a hexagonal phase to a lamellar phase. White regions represent organic domains (which contain surfactants); gray regions represent silica. d_{10} is defined for both phases. Lattice directions a , b , and c are also defined for the hexagonal phase. (b) Schematic illustrating the evolution of the surfactant packing shape within the hexagonal phase as a function of temperature and pressure. The packing parameter, g , is given by $V/(a_0l)$; V , a_0 , and l are defined in the figure. For this cartoon, $g_1 < g_3 < g_2$.

confirm the presence of a hexagonal phase that transforms to a lamellar phase at elevated temperatures. Structural differences exist between 0.001 and 1 GPa samples, however. Such differences can be observed by comparing the d spacing d_{10} , which is defined in Figure 2a and related to the lattice constant of the composite. Hexagonal d_{10} values for both samples are plotted as solid lines in Figure 3. After heating to ~ 60 °C at 0.001 GPa, the periodic repeat distance begins to increase and the relative intensity of the various hexagonal peaks begins to change. This process is usually associated with more regular hexagonal order.^{6,19–23} At 1 GPa, however, the periodic repeat distance only decreases upon heating, and the relative peak intensities do not change significantly, suggesting that this structural optimization does not occur.

The trends in d_{10} peak positions correlate with trends in the peak intensities, which have been plotted as dashed lines in Figure 3. At 0.001 GPa, increasing peak intensity is associated with structural optimization and some surfactant loss.⁶ Despite this surfactant loss, an increase in d spacing occurs with heating at low pressure because thermal excitation of the surfactant tails drives the composite toward a lower density, lower curvature

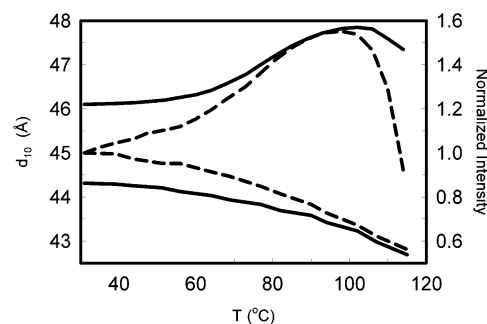


Figure 3. Comparison of d_{10} (solid lines) and normalized peak intensities (dashed lines) at 0.001 GPa (top curves) and 1 GPa (bottom curves) as composites are hydrothermally treated. At 0.001 GPa, increasing peak position and intensity indicate the development of more regular hexagonal order. The drop in initial peak position when the composite is placed under 1 GPa pressure confirms that the composite is being compressed. Decreases in peak position and intensity upon heating at 1 GPa suggest increased silica compressibility and possibly poorer hexagonal order at high temperatures.

structure.^{6,10} The 1 GPa data presented in Figure 3 show only a smooth shift to smaller d spacing with increasing temperature, indicating that formation of low-density phases cannot occur at elevated pressures. The 1 GPa data also show a slow but steady drop in peak intensity, suggesting that structural optimization cannot occur at elevated pressure and that some structural degradation may even be taking place. Note that the initial drop in peak position at 1 GPa compared to 0.001 GPa confirms that the sample is under compression.

The drop in hexagonal order at high pressure may occur because of increased silica hydrolysis. Higher pressure increases the autoionization constant for water (K_w) and therefore increases the concentration of hydroxide ions present in the mixture.^{24–26} A rise in hydroxide ion concentration can drive the hydrolysis of silica, increasing the framework's flexibility. Such increased flexibility could lower the activation barrier for the hexagonal-to-lamellar phase transition observed here.⁷ As a result, if this is the dominant factor modifying structural rearrangement under pressure, a lower phase transition temperature is expected. However, at 1 GPa, the transition midpoint temperature is found to be 159 °C, which is much greater than the 118 °C value observed for the composite at 0.001 GPa. These temperatures were determined by measuring the loss of hexagonal peak intensity and the rise of lamellar intensity and then assigning the halfway point on the rise and fall to the transition point.

TABLE 1: Determining the Internal Pressure for $g = 0.603$

T [°C]	P_{external} [GPa]	l [Å ²]	$V = C_{\text{tail}} \cdot V_{\text{C}_{17}\text{H}_{36}}$ [Å ³]	$V_{\text{head}} = C_{\text{head}} \cdot V_{\text{TETP}}$ [Å ³]	$a_0 = V_{\text{head}}^{2/3}$ [Å ²]	P_{internal} [GPa]
120	0.001	19.9	661.5	409.0	55.1	0.001
160	1.0	19.2 ^a	628.7	400.1	54.3	0.077
160	1.0	19.9 ^b	663.3	411.8	55.3	0.024

^a $l = l(T)$. ^b $l = l(T, P)$.

The results suggest that modification of transition kinetics is not the dominant change that occurs at elevated pressure.

To understand why the transition midpoint shifts to a higher temperature when the composite is placed under 1 GPa of pressure, we must understand the nature of the transition. Thermally-induced conformational disorder of the surfactant tails causes the hexagonal phase to transform to a lamellar phase (as shown in Figure 2a).^{5,8} Increased tail motion leads to changes in the effective surfactant curvature, which can be defined as a ratio of surfactant head and tail sizes.²⁷ A large head volume and small tail volume give rise to high curvature (for example, a hexagonal structure), whereas a small head volume and a large tail volume result in a low curvature structure (as in a lamellar phase).^{28,29} Therefore, modifying head and tail volumes (through variables such as chemical control, temperature, or pressure) can alter curvature. For example, recent work¹⁰ has revealed that the hexagonal-to-lamellar phase transition temperature in silica/surfactant composites can be increased by using surfactants with smaller average tail volumes. Because frustrated curvature provided the driving force for mesostructural change, a composite with a lower tail density needs more thermal excitation of the tails to possess the same curvature as a composite that starts with a higher tail density. Similarly, by adding an organic molecule that swells the tail and thus increases the tail volume, a hexagonal-to-lamellar transition can be induced in these same composites at ambient temperature.³⁰

To model the pressure effect on this curvature-driven phase transition, we consider the high-temperature compressibility of the surfactant, separating the compressibility of the quarternary ammonium headgroup (BrN(CH₃)₄) from the alkane tail (C₂₀H₄₂). Because volume measurements as a function of temperature and pressure are not available for BrN(CH₃)₄ and C₂₀H₄₂, we approximate their volumes using tetraethylammoniumtetrapropylborate (TETP)³¹ and *n*-heptadecane (C₁₇H₃₆)³² for the head and tail, respectively. Initial comparisons of TETP and C₁₇H₃₆ compressibilities reveal that the alkane chain contracts more readily than the ammonium salt when placed under high pressures, especially at elevated temperatures. Similar behavior is expected from our samples: tails should deform more than heads when compressed. Therefore, applied pressure should suppress much of the tail thermal motion and favor a higher curvature structure. Figure 2b illustrates how the packing shape and thus the curvature evolve with temperature and pressure. This basic picture supports our result of a higher transition temperature at elevated pressure; extra thermal energy is needed to increase (and overcome suppressed) tail motion.

The discussion presented above paints a qualitative picture of the pressure effects on composite transitions. By imposing Israelachvili's²⁷ definition of a geometric packing parameter g , we can quantify curvature and subsequently develop a method for estimating the internal pressure applied to the organic domains of the composite. The packing parameter, g , is given by $V/(a_0 l)$, where V is the surfactant tail volume, a_0 is the hydrophobic–hydrophilic interfacial area, and l is the effective tail length (see Figure 2b). A small g value near 0.5, for example, gives rise to high curvature structures, such as hexagonally

packed cylinders, whereas a large g value near 1 leads to low curvature structures, such as the bilayers in the lamellar phase.

In the absence of differential kinetic effects, the value of g required for the hexagonal-to-lamellar phase transition should be the same at any phase transition point, regardless of experimental conditions. This provides a well-defined transition condition that we can use to learn about the local environment within the organic domains of the composite under pressure. Specifically, we can ask the question, when the external pressure is 1 GPa, what is the effective internal pressure felt by the surfactant molecules? Previous studies using luminescent probe molecules suggest that this internal pressure will be significantly lower than the applied external pressure.⁴ In this construction, we equate the surfactant curvature at the midpoint transition temperature of the composite at 0.001 GPa to the curvature at the midpoint transition temperature of the composite at 1 GPa. In other words, $g(120\text{ °C}, P_{\text{external}} = P_{\text{internal}} = 0.001\text{ GPa}) = g(160\text{ °C}, P_{\text{external}} = 1\text{ GPa}, P_{\text{internal}} = ?)$.

The g value for the composite at 120 °C and 0.001 GPa is calculated using the values listed in Table 1. The tail volume V is the volume of *n*-heptadecane³² scaled by C_{tail} , which is the number of carbons present in a surfactant tail relative to the number of carbons in C₁₇H₃₆. The hydrophilic–hydrophobic interfacial area a_0 is estimated from surface area studies of the porous silicas derived from these silica/surfactant composites. The details of this calculation are presented elsewhere.¹⁰ The pressure and temperature dependence of a_0 is approximated using a cubic head volume, which in turn is calculated using the volume of TETP,³¹ scaled by an appropriate factor, C_{head} . The initial length l is based on molecular modeling done through Spartan;^{10,33} the data of Kirk and Grüner³⁴ are used to follow changes in the length with temperature under ambient pressures. A g value of 0.603 is found at the transition point of 0.001 GPa and 120 °C.

Using the temperature and pressure dependences of the volume data for *n*-heptadecane and TETP^{31,32} with the appropriate scaling factors allows us to tabulate the temperature and pressure dependences of V and a_0 . If the pressure dependence is assumed to arise mostly from the volume and not the length of the tail, then temperature-dependent values of l (which have no explicit dependence on pressure) can be combined with the corresponding V and a_0 values to calculate g values for various temperatures and pressures. Because we impose the constraint that the packing parameters are equal at the two phase transition points, we can use the tabulated volume data to determine what pressure at 160 °C results in a g value of 0.603 (see Table 1, second line). This pressure is the internal pressure and is found to be about 0.08 GPa.

An applied pressure, however, suppresses thermally induced fluctuations. As a result, the applied pressure should affect the tail length l as well as the tail volume. To estimate a pressure dependence for l , we use the known temperature dependence of the tail length and correlate the loss of thermal fluctuations produced at high pressure with those resulting from lowering the temperature. Specifically, the tail volume at 160 °C and elevated pressure is equated to the tail volume at 0.001 GPa

and a lower temperature. With this latter volume at 0.001 GPa and a lower temperature, a corresponding l can be calculated (as described earlier) and then used as the value for l at 160 °C and the higher pressure. Of course, this approximation does not affect the g value at 120 °C and 0.001 GPa (as listed in Table 1, first line). The internal pressure calculated in this manner, however, is much smaller and is approximated to be 0.02 GPa. Values for this calculation are also listed in Table 1, third line.

Using these two methods to calculate P_{internal} yields a range of pressures. Both methods, however, confirm that the internal pressure is significantly lower than the external pressure and indicate the silica framework supports much of the applied load.^{3,4} We also note that kinetic effects (discussed above) should only decrease the observed transition temperature at elevated pressure. A slightly higher transition temperature would correspond to a higher internal pressure, and so the values presented above are something of a lower bound. To increase our confidence in these internal pressure values, we can also estimate the internal pressure by a completely different method. Specifically, we can look at the correlation between composite volume change and the applied pressure. To do this, we use the isothermal compressibility (κ_T) to estimate the internal pressure. κ_T is defined as the fractional volume change $\Delta V/V_0$ ($=[V_{\text{highP}} - V_0]/V_0$) that results from an applied pressure ΔP ($=P_{\text{high}} - P_0$) and can be written as $-(\Delta V/V_0)/\Delta P$. Here, V_0 is the volume at the initial pressure P_0 ($= 0.001$ GPa) and V_{highP} is a volume at some greater pressure P_{high} , which can be the external or internal pressure.

We can approximate the isothermal volume compressibility for our silica/surfactant composite compressed in an aqueous medium from our low angle X-ray scattering data. To do this, we make the approximation that changes in unit cell volumes are proportional to $(d_{10}/d_0)^3$, where d_0 is the initial position (that is, at 0.001 GPa) of the fundamental diffraction peak. This approximation assumes isotropic compression of the uniaxial hexagonal composite and thus overestimates the volume compressibility.³⁵ Using this assumption, our data can be used to calculate a κ_T value, although we usually report the inverse of the volume compressibility, which is known as the bulk modulus. The current value of about 9 GPa is in good agreement with previous experiments by Wu and co-workers,³ who obtained a bulk modulus of 11 ± 3 GPa for the same type of composites compressed using argon as a pressure medium. Although the difference is not significant, we use 9 GPa as the relevant value for the bulk modulus of our composite in water, which corresponds to an 11.3% volume decrease at 1 GPa. We expect the organic phase to experience the same volume change. Determining the (internal) pressure felt by the organic domains follows if the volume compressibility of the surfactant is known.

We approximate the bulk modulus for C₂₀TAB using the literature value reported for dodecyltrimethylammonium bromide (C₁₂TAB), which has a value of 2.4 GPa.³⁶ This assumption is reasonable as comparison of fractional volume changes for C₉H₂₀ and C₁₇H₃₆ with respect to small pressure changes (~ 0.02 GPa) reveal that these two alkane chains possess negligible ($< 1\%$) differences in compressibilities.³² Therefore, a fractional volume change of -0.113 results from an internal pressure of 0.27 GPa. Instead of using the compressibility of C₁₂TAB, we can also approximate the volume compressibility of C₂₀TAB from scaled volumes of TETP and C₁₇H₃₆ at 160 °C as a function of pressure.^{31,32} This approximation indicates that a 11.3% volume decrease occurs at an internal pressure of about 0.33 GPa. The small difference between 0.27 and 0.33 GPa further supports the use of the C₁₂TAB compressibility

value for C₂₀TAB and indicates that the internal pressure is significantly smaller than the applied load of 1 GPa.

As mentioned before, the bulk modulus of 9 GPa assumes uniform compression. In hexagonal structures, however, the c axis (as defined in Figure 2a) is usually considered to be the stiffer direction, and so it may be more reasonable to assume that the compressibility in this direction more nearly approximates bulk silica (bulk modulus ~ 35 GPa).³⁷ Under an applied load, area compression that occurs within the $a-b$ plane (as defined in Figure 2a) is rigorously proportional to $(d_{10}/d_0)^2$. To determine the fractional volume change (and subsequently the internal pressure), the total volume change is simply taken as the product of the cross-sectional ($a-b$) area change and the long (c) axis linear change. The linear compression along the c axis is simply the cube root of a uniform volume compression for bulk silica. A fractional volume change of -0.086 results for our silica/surfactant composite. Combining this volume decrease with a surfactant bulk modulus of 2.4 GPa³⁶ yields an internal pressure of 0.21 GPa.

All values determined for the internal pressure are in remarkably good agreement, given the simplicity of the models. The g -based results may provide better values of the internal pressure because they account for surfactant curvature rather than just considering surfactant volume. In the confined geometric architecture of a silica/surfactant composite, volume cannot be optimized independently of curvature.^{9,10} The complexity of the phase transition data and the possibility of kinetic effects, however, adds uncertainty to these values. Combining all of the analyses done in this work suggests a true internal pressure of about 0.1 GPa. Although there is certainly some error in this value, it is clearly lower than the applied pressure of 1 GPa.

It is important to comment that, for a frustrated curvature to drive the hexagonal-to-lamellar structural change, the lamellar phase formed under pressure must have the same structure as a lamellar phase formed at lower pressure. That is to say, pressure must not cause interdigitation of the surfactant tails. Figure 3 shows that under 1 GPa of pressure the hexagonal phase is compressed and d_{10} changes by about 2 Å. The lamellar phase is slightly more compressible, with its d_{10} value dropping by about 3–4 Å (not shown). However, this change in d_{10} is not large enough for interdigitation to have occurred in the lamellar phase upon application of pressure. In fact, if we assume isotropic compression, the lamellar phase possesses a lower limit bulk modulus of about 3 GPa, which is comparable with the value (~ 2.4 GPa) obtained for pure surfactant.³⁶ If the lamellar phase is assumed to have the compressibility of bulk silica in the lamellar planes and a higher compressibility normal to the planes, we calculate an upper limit for the bulk modulus of about 8 GPa, a value similar to that obtained for the hexagonal phase. These predictable modulus values indicate that heating and compressing the composite does not result in fundamental structural changes at the atomic level, and therefore, the presence of a lamellar phase with interdigitated tails under pressure is highly unlikely.

Our results present additional evidence that the inorganic framework of periodic silica/surfactant composites provides a protective nanometer scale organic environment when the composites are subject to elevated pressure. Applying our knowledge that the hexagonal-to-lamellar phase transition is curvature-driven,^{9,10} we can consider surfactant packing as an indirect probe of the molecular environment of the organic phase and use curvature to estimate the internal pressure. More robust materials synthesized at higher temperature can have moduli

as high as 46 GPa.³ Although these materials cannot undergo a hexagonal-to-lamellar phase transition, our results suggest that the internal pressure in such composites should be very low. As a result, this class of materials has unique potential for application that require locally mild conditions in the presence of a large applied load.

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