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Phase Transitions

Reversible Switching of Lamellar Liquid Crystals into Micellar Solutions using CO_2**

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Surfactants have the ability to self-assemble into morphologically different structures, such as micelles, vesicles, and liquid crystals. The functions and properties of surfactant systems depend strongly on their microstructures. Therefore, surfactant assemblies have wider applications in different fields of chemical engineering, material science, biology, environmental science, food industry, detergents, and enhanced oil recovery.[1] Such applications are due to the desired functionalities that can be achieved by tuning the microstructures. With regular array of surfactant bilayers alternating with water layers, lamellar liquid crystals are anisotropic and highly viscous, which is very different from isotropic and much less viscous micellar solutions.[2,3] Switching the phase transition between lamellar liquid crystal (L_α) and micellar solution (L_1) is very interesting because these two kinds of surfactant assemblies are used for soaps and detergents,[4] drug delivery,[5] model membranes,[6] and as template for the synthesis of nanosized materials.[7–9] Many different methods can be used to induce the phase transition between the lamellar liquid crystal and the micellar solution, including variation of temperature and surfactant concentration, and addition of co-surfactants, inorganic salts or hydrocarbons.[10,11] However, additives, such as co-surfactants and salts, can lead to economic and environmental costs. Furthermore, contamination and/or modification of products because of additives should also be taken into consideration. Development of effective, controllable, economical, and environmentally benign methods to switch the phase transition between the lamellar liquid crystal phase and the micellar solution is therefore challenging and of great importance.

Supercritical or compressed CO_2 has received much attention in recent years because of its availability, low cost, nonflammability, and low toxicity. Compressed CO_2 has been widely used in different fields, such as extraction and fractionation,[12] chemical reactions and material science,[13,14] controlling the stability of reverse micelles,[15] induction of nanoemulsions,[16] creating microemulsions with CO_2 as continuous phase,[17–20] changing membrane fluidity and melting point of liposome system,[21] and tuning the properties of organic solvents.[22]

Herein, we present the phase transition between L_α and L_1 phases using a compressed CO_2 and AOT/water system. The possible mechanism for the CO_2-induced phase transition is also discussed. The phase diagram and microstructure of AOT/water system has previously been studied in detail.[23–25] This phase transition is very interesting from both scientific and practical points of the view. CO_2 can induce the $L_\alpha \rightarrow L_1$ phase transition at ambient temperature, whereas the phase transition occurs at or above 140 °C in the absence of CO_2 for the surfactant concentration used herein (the AOT/water binary phase diagram is shown in Figure S1 in the Supporting Information). The CO_2-induced $L_\alpha \rightarrow L_1$ phase transition is reversible, and can easily be realized by the application of and release of pressure. As the gas can be easily removed by release of pressure, the post-processing steps are easier. The conventional post-processing steps comprise removal of additives, such as co-surfactants and salts that usually cause contamination or modification of products. Furthermore, this method is environmentally benign.

We studied the phase behavior of AOT/water (1:1 by weight) lamellar liquid crystal in the presence of CO_2 at 290.7 K and at different CO_2 pressures. Figure 1 A shows photographs of the liquid crystals at different pressures. All the photographs were taken after stopping the stirrer for 30 minutes. In the low pressure range, the viscosity of the system was very high and gradually decreased with the addition of CO_2 (photographs a–c). Interestingly, as the pressure reached an optimum value, the sample suddenly lost its viscoelasticity and changed into a transparent fluid (photographs d and e). The phase transition from liquid crystal to isotropic fluid was reversible and could be repeated by controlling the pressure (photographs f and g). After releasing CO_2, the fluid solution shown in photograph d changed into the L_α phase as shown in photograph f, and the transparent fluid formed again after CO_2 was recharged (photograph g). The viscosity of the AOT/water system at different CO_2 pressures indicates a dramatic decrease in the viscosity over a narrow pressure range. However, the viscosity remained constant upon further application of pressure (Figure 1 B). This result is in agreement with the direct phase transition as observed in Figure 1 A. The pressure at which the viscosity becomes independent of pressure is termed as the phase transition pressure, P_T.

X-ray scattering is one of the most useful techniques to characterize the lamellar structure.[26] Figure 2 shows the X-ray scattering spectra of the AOT/water system (1:1 by weight) at different CO_2 pressures. In the absence of CO_2, the X-ray scattering spectrum is typical of the lamellar liquid

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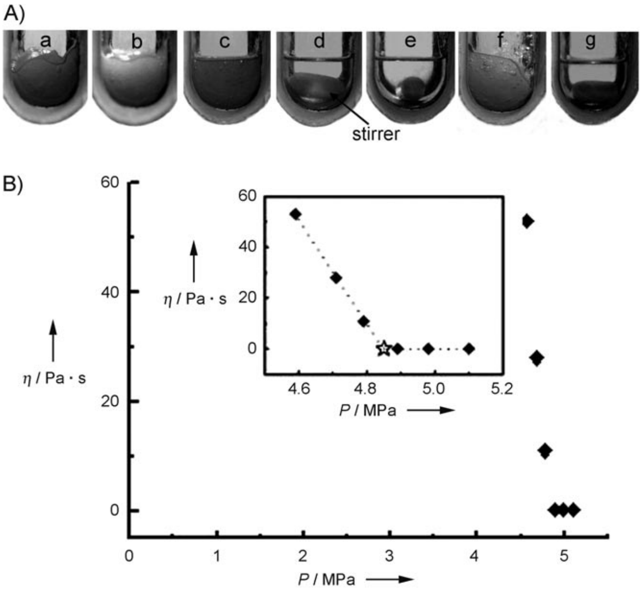


Figure 1. A) Photographs of the AOT/water system (1:1 by weight) a) without CO_2, and at CO_2 pressures of b) 3.09 MPa, c) 4.36 MPa, d) 4.85 MPa, and e) 5.07 MPa at 290.7 K. Photographs f and g correspond to d after releasing of CO_2 and pressurization to 4.85 MPa again, respectively. B) Viscosity of the AOT/water system (1:1 by weight) at different CO_2 pressures and at 290.7 K. The viscosity is too large to be determined in the pressure range of 0–4.5 MPa. The inset shows the magnified viscosity versus pressure curve in the pressure range of 4.5–5.2 MPa, where ☆ is the phase transition pressure P_T.

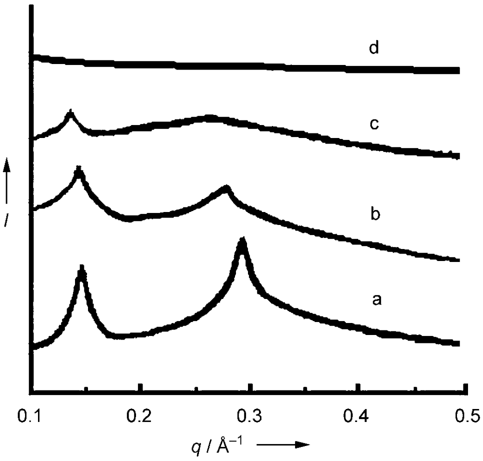


Figure 2. X-ray scattering curves of the AOT/water system (1:1 by weight) a) without CO_2 and at different CO_2 pressures of b) 2.70 MPa, c) 3.81 MPa, and d) 4.90 MPa, respectively.

crystal, with the first- and second-order Bragg peaks between 0.1 and 0.5 $Å^{-1}$, and the ratio of the relative positions q_2/q_1 is close to 1:2 (Figure 2a). The lamellar period ($d = 2\pi/q$) is 44 Å, which is consistent with literature values.[27] Upon addition of CO_2, gradual changes were observed in the scattering spectra. At pressures of 2.70 and 3.81 MPa (Figure 2b and c, respectively), the Bragg peaks moved to the lower-angle vector, corresponding to the enlarged spacing values of 46 Å and 50 Å, respectively. This result indicates that CO_2 can swell the lamellar period. In particular, at 3.81 MPa, the first- and the second-order Bragg peaks appear to be suppressed, which suggests the partial short-range disruption of the lamellar structure; however, in the long range, the lamellar structure is preserved. At 4.90 MPa, which is higher than the phase transition pressure, no Bragg peaks were observed, as expected for an isotropic solution. Thus, the results from X-ray scattering measurements give further support to the CO_2-induced phase transition from anisotropic liquid crystal to isotropic fluid. Furthermore, electrical conductivities of the AOT/water system at different CO_2 pressures were determined, which give further evidence to the $L_\alpha \rightarrow L_1$ phase transition (Supporting Information, Figure S2).

The effects of CO_2 on the AOT/water lamellae at different AOT concentrations were also studied. For AOT/water lamellar liquid crystals with AOT concentrations of 50, 60, 65, and 70 wt %, P_T increased with the increasing AOT concentration (Supporting Information, Figure S3). Furthermore, the effect of CO_2 on the AOT/water lamellae at different temperatures was studied, and an increase in P_T with increasing temperature was observed (Figure S4). This effect is most likely due to the solubility of CO_2 in the system, which according to Henry's law decreases with increasing temperature.

Surfactant assemblies have been widely used as soft templates for the synthesis of different materials.[28–30] The morphologies of the products synthesized can also reflect the microstructure of the surfactant assemblies. Therefore, we synthesized gold nanostructures in AOT/water lamellar liquid crystal and AOT/water/CO_2 micelles using the hydrophilic precursor of $HAuCl_4$. We found that the surfactant AOT can effectively reduce $HAuCl_4$, and no additional reducing reagent was required. Without the addition of CO_2, large gold plates 10–30 μm in size were formed, which can be clearly observed from the SEM and TEM images (Figure 3a, b). The electron diffraction (ED) pattern shown as an inset in Figure 3b confirms that these plates have fcc single-crystalline gold structures and have ⟨111⟩ orientation.[31,32] The formation of gold plates is consistent with the structure of the lamellar template. However, at 4.98 MPa, spherical gold particles were obtained (Figure 3c), which aggregated significantly and the size distribution is in the 3–300 nm range. This aggregation is due to the continuous phase of water under the given conditions, and the template effect of lamellae on the reduction of hydrophilic $HAuCl_4$ is com-

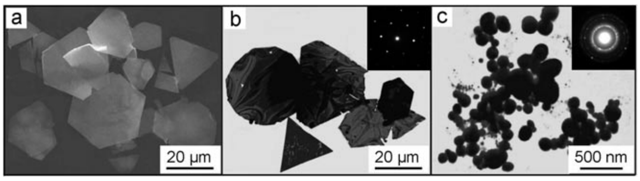


Figure 3. a) SEM and b) TEM images of gold plates prepared in AOT/H_2O lamellar liquid crystal (1:1 by weight) without CO_2. c) TEM image of gold particles prepared in AOT/H_2O/CO_2 system at 4.98 MPa. The insets of b and c are the corresponding electron diffraction patterns.

pletely lost. The ED pattern in the inset of the TEM image shows that the obtained gold particles are polycrystalline.

Apart from the gold particles, silica structures were also synthesized from AOT/water lamellar liquid crystals and AOT/water/CO_2 micelles, respectively. The hydrophobic tetraethyl orthosilicate (TEOS) was used as the silica precursor, which can provide further insights into the hydrophobic domain of surfactant assemblies. In the absence of CO_2, a small amount of hydrochloric acid was added to the AOT/water–lamellar liquid crystal containing TEOS to accelerate the hydrolysis of TEOS. Clearly, silica film was obtained without CO_2, as can be seen from the SEM and TEM images (Figure 4a, b). The film appears to be wrinkled, mainly because of their large size and small thickness. In the presence of CO_2, no additional catalyst was added, because CO_2 can dissolve in water and partially ionized to form acid ($H_2O + CO_2 = H^+ + HCO_3^{-1}$), which can be used as a catalyst for the hydrolysis reaction of TEOS.[33] At 5.50 MPa (higher than P_T), hollow silica spheres about 50–100 nm in size were obtained (Figure 4c, d). A mechanism of CO_2-in-water interface templating can explain the formation of hollow silica, similar to those formed in CO_2-in-water emulsions.[34] Thus, the synthesis of gold and silica structures serve as examples that demonstrate the tuning of morphologies in materials by inducing phase transition with compressed CO_2. Indirectly, the syntheses support the fact that CO_2 can cause the $L_\alpha \rightarrow L_1$ phase transition.

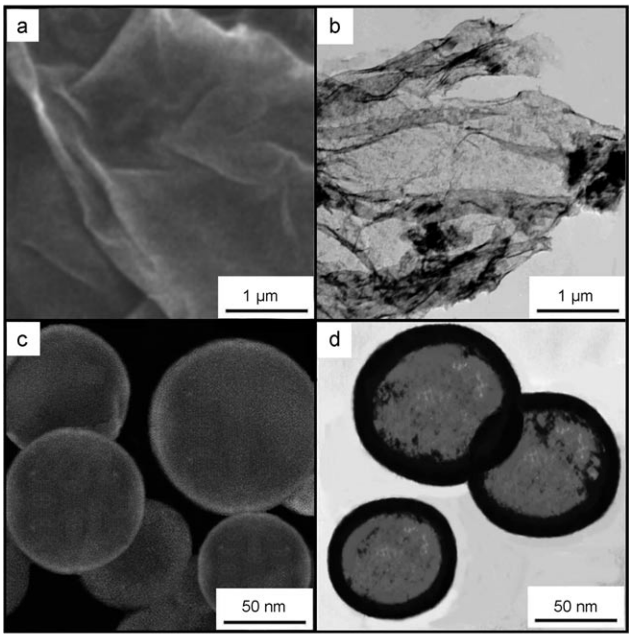


Figure 4. SEM and TEM images of silica particles prepared in the AOT/water system (1:1 by weight) without CO_2 (a and b) and at 5.50 MPa (c and d).

The mechanism for this interesting phenomenon of CO_2-switching $L_\alpha \rightarrow L_1$ phase transition is of great importance. As mentioned above, CO_2 can be ionized in water to change the acidity of water. To clarify the effect of carbonation of CO_2 with water on the $L_\alpha \rightarrow L_1$ phase transition, hydrochloric acid solutions of pH 3–7 were used to replace water in the experiment without CO_2. The system was typical of the L_α phase structure, indicating that the ionization of CO_2 in water is not the reason for the $L_\alpha \rightarrow L_1$ phase transition. It has been reported that compressed CO_2 can be inserted into the surfactant tail region of Triton X-100/cyclohexane reverse micelles, which affects the stability of the reverse micelles.[15] As CO_2 is a small nonpolar molecule, it can accumulate in the hydrophobic region of liposome bilayers and change the membrane fluidity.[21] To obtain more information on the mechanism, the effect of P_T on a series of alcohols with different alkyl chain lengths was studied. The amount of alcohol was as low as 0.02 mL/1 g (AOT + water), which does not induce the phase transition. As shown in Figure 5a, the effect of ethanol and 1-propanol, which are water soluble, have a very limited effect on the phase transition pressure. However, *n*-butanol, 1-pentanol and *n*-hexanol, of which the solubility in water is 7.7 wt%, 1.7 wt%, and nearly zero, respectively, reduce the phase transition pressure considerably, and P_T increases with the increasing alkyl chain length. It can be expected that the alcohols are distributed in between the bilayers and the water layers, the larger alcohols existing preferentially in the bilayer region. Therefore, it can be deduced that an alcohol with longer chain has more significant effect on the bilayers and has a lesser effect on the water layers. Furthermore, the effect of *n*-alkanes on the phase transition pressure was also studied (Figure 5b). The phase

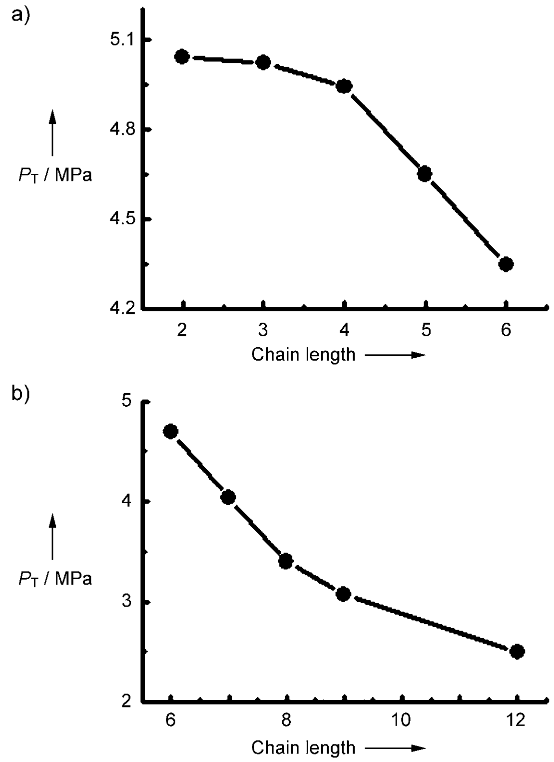
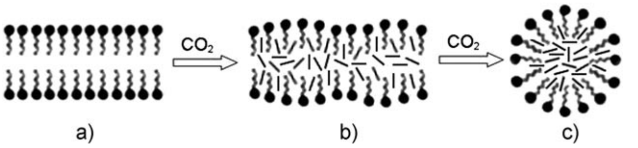


Figure 5. Phase-transition pressures (P_T) of a) AOT/H_2O/*n*-alcohol and b) AOT/H_2O/*n*-alkane at 290.7 K. The weight ratio of AOT to water is 1:1, and the volume of alcohol (or alkane) is 0.02 mL/1 g (AOT + water).

transition pressure decreases markedly with the size of the hydrocarbon chains, which can be expected as the larger alkanes have significant effects on the structure of the bilayers. All of the above studies suggest that the change of the properties of the bilayers is the main reason for the phase transition.

On the basis of the above results, we proposed a possible mechanism for the $L_\alpha \rightarrow L_1$ phase transition, which is shown in Scheme 1. In the absence of CO_2, AOT/water system is in the L_α phase region, that is, the hydrocarbon tails of the surfactant form the inner part of the bilayer, whereas the ionic heads of the surfactants are strongly hydrated by water and constitute the outer surface of the bilayer (Scheme 1a). Compressed CO_2 can easily be inserted into the hydrophobic surfactant bilayer of the lamellar L_α phase, even deep inside the tail region of the surfactant (Scheme 1b). As CO_2 is very soluble in hydrocarbons, its insertion changes the structure of the bilayers. With increasing pressure of CO_2, the ordering structure of L_α phase is disrupted, and a more thermodynamically stable micellar solution in water as a continuous phase is formed in presence of excess CO_2 (Scheme 1c). The viscosity of the micellar solution is much lower than the lamellar liquid crystal because the viscosity of water is relatively low, and water acts as the continuous phase. Insight into the detailed mechanism for this phenomenon should be studied further.



Scheme 1. A possible mechanism for the $L_\alpha \rightarrow L_1$ phase transition induced by compressed CO_2. a) Without CO_2, and at pressure b) lower and c) higher than P_T.

In summary, we found that compressed CO_2 can induce the $L_\alpha \rightarrow L_1$ phase transition of AOT/water system reversibly at ambient temperature by controlling the pressure. In the absence of CO_2, the $L_\alpha \rightarrow L_1$ phase transition temperature for the studied system is more than 140 °C. The ambient-temperature transition is advantageous because of its simplicity and low-energy consumption. The possible mechanism for this phenomenon is based on insertion of CO_2 into the hydrophobic region of the lamellae. We intend to study detailed mechanism in future. The CO_2-controlled phase transition between surfactant assemblies may have wider applications in material synthesis, polymerization, and chemical reactions.

Experimental Section

The apparatus for the phase-behavior investigation was similar to that used previously for studying reverse micelle solutions at elevated pressure.[35] In a typical experiment, the suitable amount of AOT/water mixture was added into the view cell, and the mixture was stirred. After thermal equilibrium was reached, CO_2 was charged into the view cell to a suitable pressure, and the phase behavior was observed. The high-pressure falling-ball viscometer and the procedures to determine the viscosity of AOT/water system were similar to those reported previously.[36] In a typical experiment, the suitable amount of AOT/water mixture was charged into the cylindrical viscometer. After the system had reached thermal equilibrium, CO_2 was compressed into the system until desired pressure was reached. The fall time of the falling ball was determined at equilibrium conditions, which was confirmed by the fact that the viscosity and pressure were independent of equilibration time. The viscosity of CO_2/AOT/water mixture was calculated by the equation of $\eta = K(\rho_0 - \rho)t$, where ρ_0 and ρ are the density of the falling ball and the liquid phase, respectively. t denotes the fall time of the falling ball, and K is the instrument parameter. The standard oils of different viscosities provided by National Standard Bureau of China were used for calibration. X-ray scattering experiments were carried out at Beijing Synchrotron Radiation Facility (BSRF). The X-ray wavelength used was 1.54 Å. In a typical experiment, the suitable amount of AOT/water mixture was added into the high-pressure cell. CO_2 was then charged into the system until the suitable pressure was reached. After equilibrium had been reached, X-ray scattering data were recorded.

For the synthesis of gold (or silica), the desired amount of $HAuCl_4 \cdot 4H_2O$ (or TEOS) was added into the AOT/water mixture (1:1 by weight), and CO_2 was charged into the autoclave to the desired pressure under stirring. After reaction for 24 h, CO_2 was released. The products were separated by centrifugation and washed by ethanol for several times. For comparison, gold and silica were also synthesized in the absence of CO_2. The SEM images were taken on a scanning electron microscopy (SEM, Hitachi-530). The TEM images and ED pattern were recorded on a JEOL JEM-2010 transmission electron microscopy operating at 200 kV.

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