

Ordering in Surfactant Mixtures Induced by Polymers

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We studied ternary mixtures of nonionic surfactant ($C_{12}E_6$, *n*-dodecyl hexaoxyethylene glycol monoether), polymer (PEG, polyethylene glycol), and water. A small amount of PEG induces demixing into the polymer-rich and surfactant-rich phases in the ternary PEG/ $C_{12}E_6$ /water mixture. Above a certain concentration and/or molecular weight of PEG, the surfactant-rich phase orders, even in a solution consisting of a few percent of surfactant. The phase boundary acts as a semipermeable membrane, and the equilibrium is determined by the chemical potential of water in two phases. The explicit expression for the amount of PEG needed to order $C_{12}E_6$ water solution is given and verified experimentally. The analysis of the coexistence conditions leads to the conjecture that only two oxygen atoms in the outward part of the hydrophilic surfactant head strongly affect the chemical potential of water. Our methodology is generic, i.e., on the same basis one can design a similar experiment for any surfactant/polymer/water system and find the right proportions of polymer that induce order in a surfactant-rich phase.

1. Introduction

The formation of complex self-assembled materials is based on the phase separation/ordering processes.^{1–4} The separation process is related to the solubility,⁵ i.e., the ability of a substance to form a solution with another substance. “Similia similibus solvuntur” (“like dissolves likes”) is the oldest rule of solubility. This rule can be a very good guide in the study of mixing and phase separation, provided one can precisely define what degree of likeness is in a given case. The chemical composition is certainly the first element that has to be considered in this context. However, with the advent of self-assembled phenomena it appears that geometrical structures formed in a self-assembling system have to be taken into account in the context of solubility.

The simplest example of the geometrical incompatibility of structures is provided by mixtures of colloids and nonadsorbing polymers in a common good solvent. It is now generally accepted that phase separation in the mixture is induced by depletion interactions. The idea of such nonspecific, geometrical interactions was introduced by Asakura and Oosawa⁶ and Vrij.⁷ There is a zone around each colloidal particle that cannot be penetrated by the center of mass of a polymer molecule. The size of the zone is proportional to the radius of gyration of a polymer. The polymer cannot penetrate the zone because such penetration would result in a great loss of its conformational entropy. If two zones overlap, then there is an imbalance of osmotic pressures that pushes the colloids together and finally results in the phase separation into the colloid-rich phase and polymer-rich phase.⁸ The effect found immediate application in the crystallization of proteins, namely, the polymers (e.g., PEG) added to protein solutions act as the precipitating agents, which induce a phase separation⁹ and finally crystallization of

proteins. In fact, the depletion forces bring the protein solution into the crystallization slot¹⁰ (where the second virial coefficient of proteins is small and slightly negative). It was observed that the proper conditions for the crystallization of proteins occur near the liquid–liquid critical point (where the protein solution demixes into two liquid phases). It was discussed by Wolde and Frenkel that crystallization is enhanced near the critical point by the critical fluctuations, which reduce the nucleation barrier.^{11,12} A crucial aspect in the phase separation and appearance of a “liquid” phase (protein-rich phase) is the range of attractive interactions¹³ between the proteins. The liquid phase appears when the ratio of the range of attraction to the range of repulsion potential is 0.3. In the mixtures of proteins and polymers, this ratio for the interactions between the proteins is set by the ratio of the radius of gyration of the polymers to the radius of the protein. On this basis, one can rationally design conditions in the solution for the proper crystallization of proteins. In the present paper, we concentrate on the ordering induced by polymers in the surfactant solutions and ask the following general question: *can we design the conditions for which the solution of polymers and surfactants exhibits ordering?* The specific question of this paper is as follows: how much PEG is needed to order even a highly dilute $C_{12}E_6$ water solution? The theoretical predictions that we obtained are verified in the experiment.

The plan of this paper is as follows. In the next section, we describe our experimental procedures. In section 3, we shortly describe separation of the $C_{12}E_6$ -rich phase from the PEG-rich phase. Section 4 contains the main results, i.e., an analytical formula for the amount of PEG needed to order a $C_{12}E_6$ -rich phase. Conclusions are contained in section 5.

2. Experimental Section

We have used the nonionic surfactant $C_{12}E_6$ (hexaethylene glycol monododecyl ether), purchased from Fluka, of purity

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better than 98% (checked on the thin-layer chromatography (TLC)). The melting temperature given by Fluka Chemical Co. for pure $C_{12}E_6$ was between 27 and 28 °C, and our measurement using differential scanning calorimetry gave 27.11 °C. The molecular weight of the surfactant is 450.66. The polymer PEG (poly(ethylene glycol)), of HPLC grade, was purchased from Merck. The molecular masses of PEG were 300, 400, 6000, and 20 000. Water was distilled, filtered, and degassed. We also ultracentrifuged the samples before measurements since in this way we could remove even tiny gas bubbles from solutions.

The mixtures were prepared at room temperature in a humid atmosphere in order to avoid evaporation of water. From the prepared mixture, we have made thin samples in the following way. First, a drop of solution was placed on a glass plate (cleaned in ultrasound cleaner and washed in acetone and methanol). Next, it was covered by the second glass plate. To control the thickness, we have placed a copper wire spacer of known thickness between two glass plates. We made samples of two thicknesses: 90 and 15 μm . Finally, the samples were sealed with the glue "Poxipol" in order to avoid the evaporation of water during the measurements. These samples were used for the optical microscopy and static light scattering measurements. For the differential scanning calorimetry, the samples were sealed in a specially sealed container.

The phase transitions in the system were studied by three different methods: optical microscopy and analysis of textures, differential scanning calorimetry, and light scattering.

Optical microscopy measurements were performed using the Nikon Eclipse E 400 microscope with crossed polarizers, equipped with the heating/cooling stage LINKAM THMS 600. The temperature was controlled up to 0.01 °C, and the sudden jump in temperature (10–30 °C) took only 30 s. The texture analysis was used to study the phase transitions in the mixtures.

Differential scanning calorimetry (DSC) measurements were made using a Calvet TG-DSC111 (Setaram, France) thermal analysis system. The samples were placed in stainless steel crucible and covered with a stainless steel cover, which was crimped with aluminum seal in order to minimize the humidity influence on the probe under study. The empty stainless steel crucible, prepared in the same way as probe, was used as the reference in all measurements. All measurements were made differentially with scan rate of 1 °C/min and temperature ranging from 10 to 70 °C.

We performed also the light scattering experiments for the cloud point measurements, supplementary to the optical microscopy. The scattered intensity was detected on a linear array of 512 photodiodes. We used the standard laser (He–Ne, 5mW) of $\lambda = 632.8$ nm and a parabolic mirror to reflect the scattered intensity toward the array of photodiodes. The temperature in this experiment was controlled up to 0.01 °C, and the typical time for the stabilization of the temperature after a sudden change was 30 s. Before the measurements, the samples were annealed at 5 °C overnight. Next, the samples were heated to higher temperatures above the phase separation temperature. The separation process was very fast at the beginning, and thus the measurements were taken every 0.5 s. The cloud point measurements using light scattering give the location of the transition temperature.

The phase diagrams of PEG/water and surfactant/water binary mixtures are well-known. High molecular weight PEG mixes with water in all proportions¹⁴ for temperatures between 0 and 100 °C. For a low molecular weight PEG and water mixture, the upper critical temperature is ca. 96–98 °C. The light scattering experiments and viscosity measurements used to

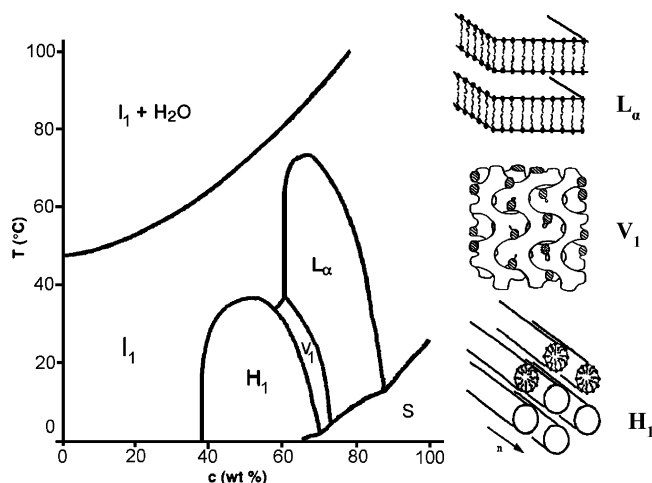


Figure 1. Sketch of the $C_{12}E_6$ /water phase diagram. The hexagonal (H_1), lamellar (L_α), and cubic-gyroid structures (V_1) are sketched as well.

determine the radius of gyration of PEG in water¹⁵ led to the following formula for the polymer radius of gyration as a function of molecular weight M_w : $R_g = 0.2M_w^{0.58}$, where R_g is given in Å. For PEG 6000 (polymerization index 136), we find $R_g = 31$ Å. PEG molecules have the hydrodynamic radius, R_h , roughly 30% smaller than R_g as determined by the dynamic light scattering.¹⁵ We have done the dynamic light scattering for PEG 6000 and found $R_h \approx 19$ Å.

The phase diagram of $C_{12}E_6$ and water is shown^{16,17} in Figure 1. The precise calorimetric study of the diagram has been done recently.¹⁸ The surfactant is miscible with water in the whole range of concentrations up to 38 wt % of $C_{12}E_6$ and for temperatures between 0 and 50 °C. Although the phase diagram was established relatively easily, the structure of the isotropic mixture of H_2O and $C_{12}E_6$ has been a matter of some controversy for a long time.^{19–26} At very low concentrations and low temperatures (below 20 °C and below 0.1% of surfactant by weight), we expect spherical micelles^{19–21} in the system. At higher concentrations, micelles grow in length^{22–25} and eventually form a network²⁶ at concentrations close to the isotropic–hexagonal phase transition, which occurs at 38 wt % of surfactant (Figure 1). The growth of micelles at high temperatures (close to the phase separation indicated in Figure 1) is affected by the critical fluctuations.^{19,21} From the measurements of the thickness of the $C_{12}E_6$ film adsorbed on amorphous silica surfaces from water solutions, one can estimate the typical size of the molecules inside a bilayer or micelle.²⁷ The overall thickness of the bilayer was found equal to 50 Å, and the area per headgroup was 40–50 Å². The X-ray scattering^{28,29} performed on the hexagonal phase indicates that the diameter of the columns in this phase is 44 Å, and the size of the unit cell is 58–60 Å. Therefore, the average size of the molecule in the bilayer is 25 Å and in the hexagonal column 22 Å.

We have studied the PEG 6000/surfactant binary mixture (Figure 2) by DSC and optical microscopy. Below 27 °C, the crystalline phase consists of PEG crystallites and surfactant crystallites. Above this temperature, the crystals of surfactant melt, and the system consists of PEG crystals and surfactant liquid. It seems that crystalline PEG does not dissolve in the surfactant liquid. As we raise the temperature above 60 °C, PEG melts, and we obtain a homogeneous liquid mixture. In the liquid state, PEG and surfactant mix in all proportions.

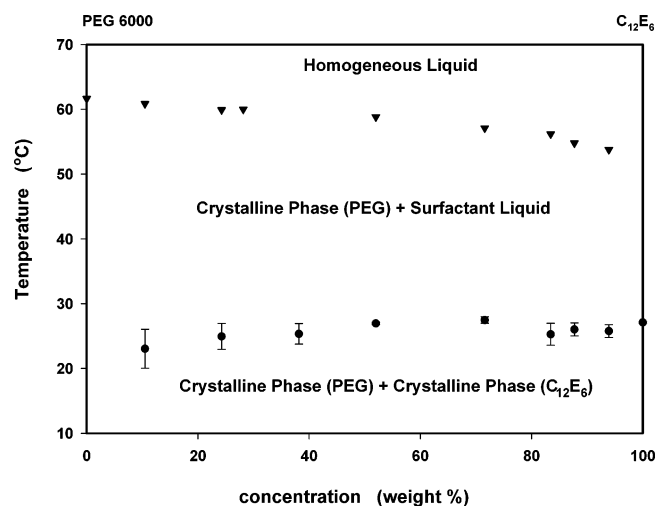


Figure 2. PEG/ $C_{12}E_6$ phase diagram obtained by differential scanning calorimetry and optical microscopy. At low temperatures, the solid phase of PEG and the solid phase of the surfactant coexist. Above 27 °C, the surfactant crystal melts, and above 60 °C, PEG melts. In the liquid state, surfactant and polymer mix in all proportions. The triangles show the melting line of PEG while circles show the melting line of the surfactant.

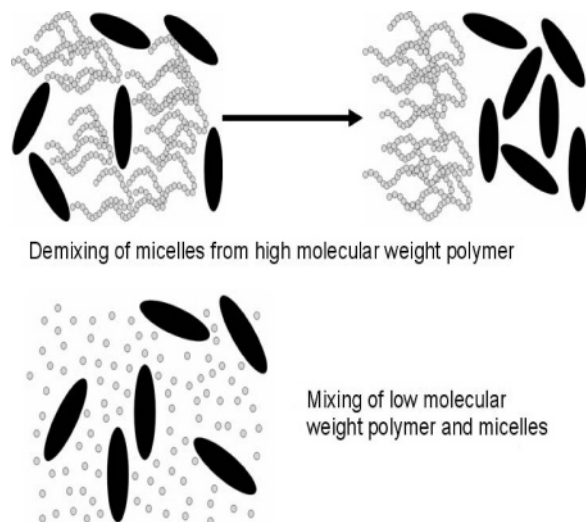


Figure 3. Schematic representation of the phase separation process in a three component mixture of the surfactant (in the form of micelles), PEG, and water. In the system of the low molecular weight polymer, the separation process does not occur due to the very short range of the polymer-induced attractive interactions.

3. Phase Separation in a Three Component Mixture at Low Concentrations

The binary surfactant/water mixture phase separates at temperatures higher than 50 °C (Figure 1), and the separation temperature depends weakly on the surfactant concentration over a wide range of concentrations. The origin of this phase transition is due to the dehydration of the surfactant heads^{30–32} and the progressive increase of the influence of the van der Waals attraction between surfactant micelles. It follows from the phase diagram that the system separates into almost pure water and concentrated surfactant solution. Adding PEG to the binary mixture induces the depletion interactions and thus changes the mechanism of phase separation. In Figure 3, we show schematically the separation process in a micellar/polymer/water system. The transition is induced by the depletion (attractive) interactions between the micelles. The Asakura–

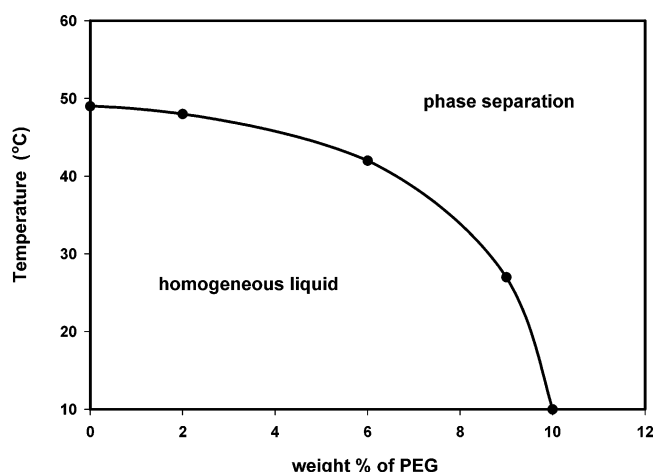


Figure 4. Temperature versus the concentration of PEG 6000 for the 3% surfactant/water mixture showing the boundaries of the homogeneous ternary mixture. The solid circles are the experimental points, and the solid line has been added as a guide.

Oosawa theory of depletion interactions has been recently confirmed experimentally for the system with a nonionic surfactant, PEG, and water mixture.³³ It followed from the experiment³³ that the micelles can be treated as hard colloidal particles. The theory of depletion-induced separation predicts that the transition very strongly depends on the ratio, $r = R_g/R$, of the polymer radius of gyration to the radius of colloidal particle (proteins, micelles, etc.). This size ratio controls the range of attractive interaction. For the size ratio of $r < 0.3$ (short-range attraction), phase separation in the liquid state does not occur, and we only have a transition from the solution to the colloidal crystal^{13,34,35}. For a larger r value, the colloid/polymer/water system separates into colloid-rich and polymer-rich water solutions. Thus for long-range attractive forces (i.e., long polymers), we expect the strong influence of polymers on the phase separation process, while for short chains the effect should be small. This is exactly what we find in the experiments. Assuming that the micelle size is $R \approx 25$ Å, we find $R_g/R \approx 0.25$ for PEG 400 and 1.24 for PEG 6000. For very short chains (PEG 300 and 400), the polymer practically does not change the transition temperatures, while for long chains (PEG 6000 and PEG 20 000), the effect is very strong (e.g., Figure 4).

4. Ordering in Surfactant Mixtures Induced by PEG: Theoretical Predictions and Experimental Verification

The ordered phases in the $C_{12}E_6$ /water binary mixture occur for concentrations of $C_{12}E_6$, $c_s^{\min} \geq 38$ wt % (Figure 1) and $T > 0^\circ\text{C}$. For $c_s < c_s^{\min}$, the mixture is homogeneous and isotropic. Adding PEG to the surfactant mixture induces a phase separation into the isotropic PEG-rich and surfactant-rich phases. The problem that we pose in this section is as follows. We mix three components PEG, $C_{12}E_6$, and H_2O , whose masses are m_{PEG} , $m_{C_{12}E_6}$, and m_{H_2O} , respectively ($c_s = m_{C_{12}E_6}/(m_{H_2O} + m_{C_{12}E_6})$). How much PEG should we add to the mixture to order the surfactant-rich phase?

We consider two coexisting phases: PEG-rich and surfactant-rich. First of all, we assume that the PEG molecule of radius of gyration, R_g , is larger than the size of the water channels, l_{H_2O} , so that in the surfactant-rich phase PEG cannot enter these channels. This is true for high molecular mass polymer and ordered surfactant phase, e.g., $R_g = 31$ Å for PEG 6000 and

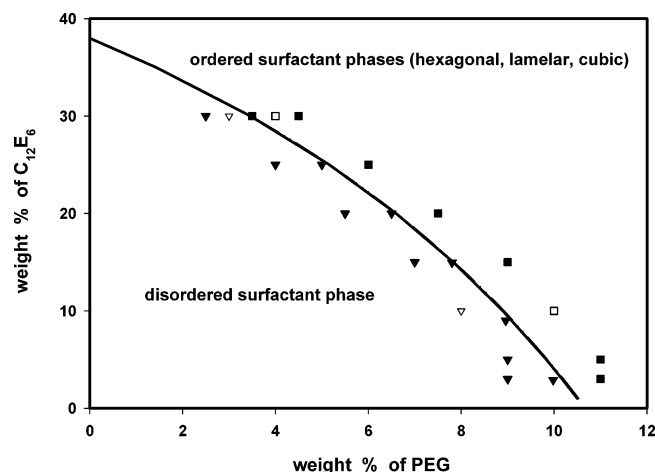


Figure 5. Weight concentration of PEG versus the weight concentration of $C_{12}E_6$ with respect to the total amount of water in the ternary PEG/ $C_{12}E_6$ /water mixture showing the regions where the separated surfactant-rich phase orders. The filled symbols are for PEG 6000, and the empty symbols are for PEG 20 000. The squares show where the surfactant-rich phase separated from the polymer-rich phase is hexagonally ordered, while triangles show the places where the surfactant-rich phase is disordered. The solid line is the theoretical curve given by eq 8. It separates the region of the disordered surfactant-rich phase from the region of the ordered surfactant-rich phase. The temperature for which the ordered phases exist are given in Figure 1. PEG does not change them. In all cases, the PEG-rich phase is disordered.

$l_{H_2O} \leq 14 \text{ \AA}$ in the hexagonal phase. It is certainly not true for PEG 300 or PEG 400. Second, the PEG-rich phase should contain very little or no micelles at all. This is a reasonable assumption since PEG forms a semidilute solution, where polymer chains overlap forming a transient network. Such a network is not easily penetrated by large micelles. In fact, we have checked this assumption using dynamic light scattering. We found that the PEG-rich phase does not contain any micelles at all. It follows that the interface between two coexisting phases acts as a semipermeable membrane,³⁶ i.e., it is permeable to water molecules only. Therefore, the thermodynamic equilibrium in the system is set by the equality of the chemical potential of water in two phases

$$\mu^I(T, p, x_1) = \mu^{II}(T, p, x_2) \quad (1)$$

where T is the temperature, p is the atmospheric pressure, x_1 is the mole fraction of water in the PEG-rich phase, and x_2 is the mole fraction of water in the $C_{12}E_6$ -rich phase. In both phases, the mole fraction of water is close to 1. The chemical structure of the PEG molecules and of the surfactant head is very similar, as they consist of OCH_2CH_2 groups. It means, in particular, that the microscopic interactions between water/polymer and water/surfactant heads are the same. Presumably, the most important part in the group are oxygen atoms, as they form hydrogen bonds with water. Thus, we may safely assume that the main part of the interactions influencing the chemical potential is due to the direct interaction of water and oxygen atoms in the surfactant heads or PEG chains. However, there is one difference between PEG in solution and $C_{12}E_6$ in the ordered phase. In the PEG solution, water has an easy access to every oxygen atom in the chain while in the ordered surfactant phase water cannot fully penetrate into the surfactant bilayer. Let us assume that the chemical potential of water strongly depends on the interactions with only Z oxygen atoms in the surfactant layer. Z will be the fitting parameter in our equations. Let Y denote the number of oxygen atoms in the PEG chain ($Y =$

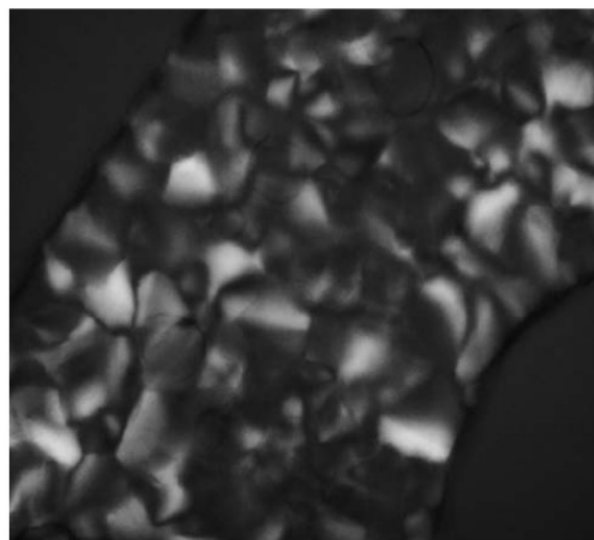
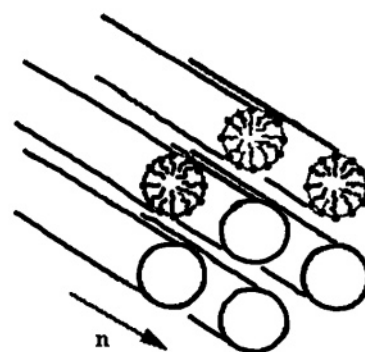
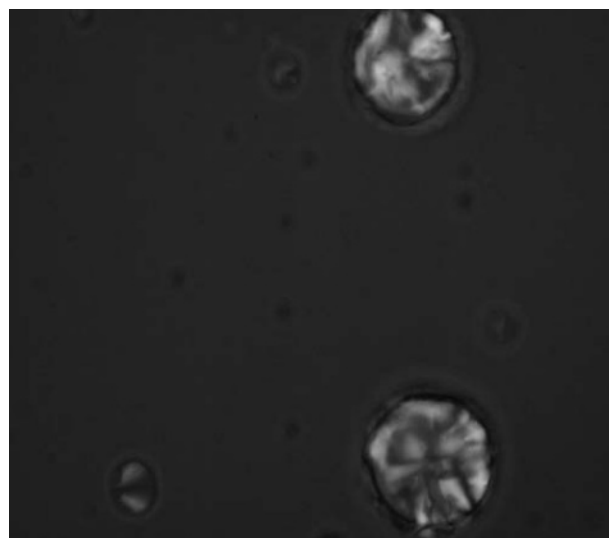


Figure 6. Both photographs show the texture of the hexagonal phase coexisting with the PEG-rich phase (black region). The photographs were obtained from the optical microscopy under crossed polarizers. The top photograph shows the hexagonal phase in the ternary mixture of 3% of surfactant and 30% of PEG (weight fractions with respect to the total amount of water in the system). Because the amount of surfactant is very small, the hexagonal phase is in the form of droplets. Below, we show a texture of the hexagonal phase in the mixture of 10% PEG and 20% surfactant. Here the ordered hexagonal phase is in the form of large domains.

137 for PEG 6000), $x_{O/PEG}$ denote the mole fraction of oxygen atoms in PEG molecules with respect to water in a PEG-rich phase, and $x_{O/C_{12}E_6}$ denote the mole fraction of oxygen atoms in $C_{12}E_6$ with respect to water in the ordered $C_{12}E_6$ -rich phase. We conjecture that the equality of the chemical potential of

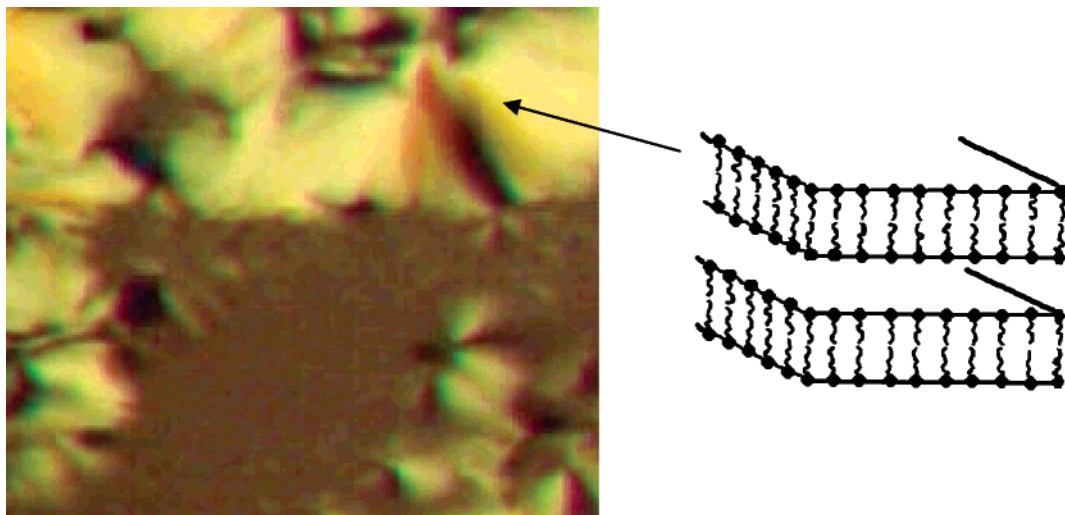


Figure 7. Photograph obtained from the optical microscope under crossed polarizers showing the texture of the lamellar phase (light region) coexisting with the PEG-rich phase (dark region) for 10% surfactant and 36% PEG.

water leads to the following condition

$$Yx_{\text{O/PEG}} = Zx_{\text{O/C}_{12}\text{E}_6} \quad (2)$$

Equation 2 simply states that the number of water molecules per one oxygen atom accessed by water (Y and Z factors) should be the same in both coexisting phases in order to equilibrate the system. This assumption holds when we have sufficient amount of water in the system but breaks down for the inverse phases in very concentrated solutions.

On the basis of eq 2 and Figure 1, we can predict the amount of polymer needed to order the surfactant mixture. From Figure 1, we find that we need at least $c_s^{\min} = 38$ wt % of surfactant in the surfactant-rich phase to get an ordered (hexagonal) phase. Thus, when the mixture separates into the PEG-rich and the C_{12}E_6 -rich phase, the ordering occurs in the latter phase when the weight fraction of the surfactant in this phase is larger than or equal to $c_s^{\min} = 38\%$. Now we want to compute the mass of PEG, m_{PEG} , of molecular weight M_{PEG} , which has to be added to the binary solution of C_{12}E_6 /water of concentration c_s by weight to induce order in the surfactant-rich phase after the phase separation. The molecular mass of C_{12}E_6 is denoted by $M_{\text{C}_{12}\text{E}_6}$ and the total mass of C_{12}E_6 in the mixture by $m_{\text{C}_{12}\text{E}_6}$. The final composition of the surfactant-rich phase is c_s^{\min} , and the final composition of the PEG-rich phase is $m_{\text{PEG}}/(m_{\text{PEG}} + m_{\text{H}_2\text{O}}^{\text{PEG}})$, where $m_{\text{H}_2\text{O}}^{\text{PEG}}$ is the total mass of water in the PEG-rich phase. Water will be divided into two coexisting phases according to eq 2. The total mass of water in the system is given by

$$m_{\text{H}_2\text{O}} = \frac{m_{\text{C}_{12}\text{E}_6}(1 - c_s)}{c_s} \quad (3)$$

and the amount of water in the surfactant-rich phase after the addition of PEG is

$$m_{\text{H}_2\text{O}}^{\text{order}} = \frac{m_{\text{C}_{12}\text{E}_6}(1 - c_s^{\min})}{c_s^{\min}} \quad (4)$$

The conservation of the mass of water gives

$$m_{\text{H}_2\text{O}}^{\text{order}} + m_{\text{H}_2\text{O}}^{\text{PEG}} = m_{\text{H}_2\text{O}} \quad (5)$$

Rewriting eq 2 in terms of the masses of the two components, we find

$$Y \frac{m_{\text{PEG}}}{m_{\text{H}_2\text{O}}^{\text{PEG}}} \frac{M_{\text{H}_2\text{O}}}{M_{\text{PEG}}} = Z \frac{m_{\text{C}_{12}\text{E}_6}}{m_{\text{H}_2\text{O}}^{\text{order}}} \frac{M_{\text{H}_2\text{O}}}{M_{\text{C}_{12}\text{E}_6}} \quad (6)$$

Combining eqs 5–8, we find the following equation for the mass of PEG

$$m_{\text{PEG}} = \frac{Z}{Y} \frac{M_{\text{PEG}}}{M_{\text{C}_{12}\text{E}_6}} m_{\text{C}_{12}\text{E}_6} \left(\frac{c_s^{\min}(1 - c_s)}{c_s(1 - c_s^{\min})} - 1 \right) \quad (7)$$

This equation does not practically depend on the molecular mass of PEG, since for high molecular masses M_{PEG}/Y is practically constant. However, PEG must have a sufficiently high molecular mass, such that a PEG molecule cannot enter the water channels of size $l_{\text{H}_2\text{O}}$ in the ordered phase. The factor Z is the only fitting parameter in eq 7. Finally, eq 7 can be rewritten in terms of the PEG weight fraction with respect to the total mass of water, $m_{\text{H}_2\text{O}}$, $c_{\text{PEG}} = m_{\text{PEG}}/(m_{\text{H}_2\text{O}} + m_{\text{PEG}})$. We get

$$\frac{c_{\text{PEG}}}{1 - c_{\text{PEG}}} = \frac{Z}{Y} \frac{M_{\text{PEG}}}{M_{\text{C}_{12}\text{E}_6}} \left(\frac{c_s^{\min}}{(1 - c_s^{\min})} - \frac{c_s}{(1 - c_s)} \right) \quad (8)$$

In Figure 5, we plot $c_{\text{PEG}} = m_{\text{PEG}}/(m_{\text{H}_2\text{O}} + m_{\text{PEG}})$ versus c_s according to eq 8 together with the experimental points. The theoretical curve divides the diagram into two regions. In one of the them, the surfactant-rich phase is ordered, and in the other, it is disordered. Fitting eq 8 to the experimental points yields $Z = 2$. The very good agreement between theory and experiment for PEG 6000 and PEG 20 000 supports the conjecture (eq 2). In Figure 6, the photographs of the textures of hexagonally ordered surfactant phase in the PEG-rich matrix is given, and in Figure 7, a texture of the lamellar phase is shown also in the PEG-rich matrix. At sufficiently high temperature, the hexagonal phase undergoes the transition to the disordered phase at the same temperature as in the binary surfactant/water mixture.

For masses of PEG smaller than m_{PEG} given by eq 7, the ternary mixture separates into the two isotropic phases. For the mass of PEG larger than m_{PEG} given by this equation, the surfactant-rich phase is ordered. This equation is valid for $c_s \leq c_s^{\min}$. When the concentration of surfactant c_s approaches c_s^{\min} ,

m_{PEG} goes to zero as expected. The equation is not valid for vanishingly small amounts of surfactant. As far as the temperature dependence is concerned, we simply note that the transition of the ordered hexagonal phase into the disordered phase occurs at the same temperature as for the pure surfactant solution, and ordered phases exist for temperatures above 0 °C. Our formula does not practically depend on the molecular mass since $M_{\text{PEG}}/Y = 44$ is constant for high molecular weight polymers.

5. Conclusions

From the analysis of many surfactant systems such as sodium dodecyl sulfate, sodium decanesulfonate, C_nE_m , dodecyl methyl sulfonate diimine, dodecyl dimethyl phosphine oxide, dodecyl diethyl phosphine oxide, dedecanesulfonic acid, tetramethylammonium dodecanoate, *N*-dodecyl-*N,N*-dimethylammonioacetamide, and many others, one finds that there is a minimum concentration of surfactant c_s^{min} usually of the order of 40% for which the binary system exhibits ordering³⁷ above 0 °C. PEG can induce order in these surfactant solutions for much smaller surfactant concentrations, and equations similar to eq 7 can be derived based on the knowledge of the chemistry of the system.

In the aforementioned surfactant systems, one could try to estimate the equilibrium conditions in the separated phases similarly as in eq 2, i.e.,

$$\alpha Y x_{\text{polymer}} = \gamma Z x_{\text{surfactant}} \quad (9)$$

where x_{polymer} is the mole fraction of the active groups in the polymer molecule that affect the chemical potential of water and $x_{\text{surfactant}}$ is the mole fraction of active groups in the surfactant molecule that affect the chemical potential of water (the mole fraction is with respect to water content in each phase separately), Y is the number of these groups in polymer, and Z is the number in a surfactant head; α and γ are two parameters denoting different interactions of the active groups in polymer and in surfactant with water. Please note that one could reduce the number of parameters to only one, i.e., $\alpha Y/\gamma Z$. For the same active groups in the polymer and surfactant, as is the case in our paper, we have $\alpha = \gamma$. The ionic surfactants and ionic polymers would introduce another complication beyond simple geometrical restrictions. The thermodynamic equilibrium in this case would be set not only by the chemical potential of water but also by the chemical potential of counterions. However, for ionic surfactants and nonionic polymers we could still use a similar equation to eq 9, but apart from the active groups, we should also include the influence of the counterions on the chemical potential of water. Probably additional interaction parameters should be introduced to account for the free counterions in water.

Finally, we would like to point out that water can penetrate the surfactant heads up to the region of hydrocarbon tails,³⁸ but this fact does not mean that all the oxygens in the head similarly affect the chemical potential. From our model, it follows that

the chemical potential of water is strongly affected by two oxygen atoms in the surfactant head. Further studies of the water activity in surfactant solutions are needed to elucidate this point.

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