

Heat-Induced Phase Transitions from an Aqueous Solution to Precipitates in a Poly(sodium 4-styrenesulfonate)/Tetradecyltrimethylammonium Bromide System

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Abstract: For the first time, temperature-induced phase transitions upon heating and cooling an aqueous solution that contained oppositely charged polyelectrolyte and surfactant mixtures was observed. The phase transition from micelles to vesicles, then to the coexistence of vesicles and superstructures that have the morphology of melon seeds, and finally to precipitates

was determined by means of turbidity measurements and transmission electron microscopy images. These phase transitions were shown to be reversible and reproducible after several heating

and cooling cycles were performed on the same sample. The novel observations for the temperature-induced phase transition from primary aggregates, such as micelles, to superstructures (i.e., vesicles) should provide new understanding for surfactant sciences, and in particular for self-assembled amphiphilic systems.

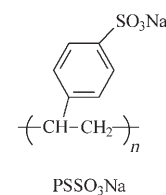
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Self-assembly and phase transitions in aqueous solutions of polyelectrolytes and surfactants have been studied extensively because they have been widely used in many diverse fields, such as demulsification systems for petroleum, templating media in materials synthesis, and as drug delivery and release systems in the pharmaceutical industry.^[1–3] Various stable structures from mixtures of polyelectrolytes and surfactants in aqueous solutions have been observed. Typical aggregates obtained from polyelectrolyte and surfactant mixtures in aqueous solutions include mixed micelles, vesicles, lamellar structures, and an L₃ phase (sponge phase).^[4] Temperature control plays an important role in the self-organization of soft materials and in phase transitions. A

simple way to control the properties and aggregation of a polymer, and in particular, phase transitions is to control the temperature. Temperature has a large effect on block copolymers, such as triblock copolymers of type (EO)_x(PO)_y(EO)_x, or nonionic surfactant solutions. Traditionally, at higher temperatures, aggregates with larger aggregation numbers could transform into primary aggregates, such as the transition from vesicles to micelles,^[5–7] that is, the aggregate size normally becomes smaller as the temperature increases. The reverse process, going from small self-assembled aggregates to larger ones, has rarely been reported.^[8–13] Recently, Huang and co-workers have reported this reverse process in aqueous solutions that contain cationic and anionic surfactants in which there is a temperature-induced micelle-to-vesicle transition.^[14,15] However, the big challenge remains to determine vesicle aggregation numbers by means of laser-light scattering.

Herein, we report phase transitions induced by means of heating the samples to transform micelles into vesicles in aqueous solutions of oppositely charged polyelectrolyte and surfactant mixtures, followed by the coexistence of vesicles and aggregates that have the morphology of melon seeds, and finally the formation of precipitates.

A concentration of 1.0 wt % poly(sodium 4-styrenesulfonate) (PSSO₃Na, *M*_w = 70000, Aldrich) in water was employed throughout this study. The aqueous



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PSSO₃Na solution was mixed with various concentrations of cationic surfactant (tetradecyltrimethylammonium bromide, TTABr), and the phase behavior was observed after the solution was allowed to equilibrate for four weeks at (25.0 ± 0.1) °C in a biochemical incubator. Increasing the concentration of TTABr (c_{TTABr}) in an aqueous solution of PSSO₃Na (1.0 wt %) allows one to observe a clear L₁ phase (micellar solution) at $c_{\text{TTABr}} \leq 34.0 \text{ mmol L}^{-1}$ and (25.0 ± 0.1) °C. After the L₁ phase, a two-phase region consisting of the L₁ phase and precipitate emerged in which the L₁ phase is at the top of the sample. We observed the novel phase-transition phenomena at a narrow TTABr concentration range of 30.0 to 34.0 mmol L⁻¹ upon heating an L₁ phase solution of a mixture of oppositely charged PSSO₃Na and TTABr molecules. As the temperature increased, an apparent phase transition is observed as the solution changes from clear, colorless to clear, sky blue, then to opaque, sky blue, and finally to opaque, milk white, as shown in Figure 1.

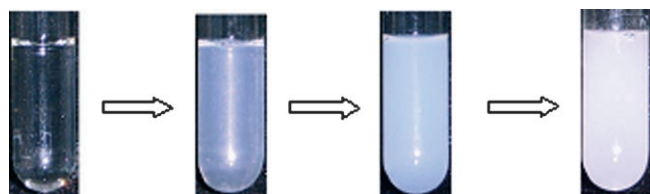


Figure 1. Apparent phase transitions of an aqueous solution of PSSO₃Na (1.0 wt %) containing TTABr (30.0–34.0 mmol L⁻¹) as the temperature was increased. a) Clear, colorless solution; b) clear, sky-blue solution; c) opaque, sky-blue solution; d) opaque, milk-white solution.

We focused our investigations on an L₁ phase solution that contained fixed concentrations of PSSO₃Na (1.0 wt %) and TTABr (32.5 mmol L⁻¹). At room temperature, the interaction between PSSO₃Na and TTABr was studied by means of ¹H NMR spectroscopic measurements. Figure 2a and b show the spectra for solutions of PSSO₃Na (1.0 wt %) and TTABr (32.5 mmol L⁻¹) in D₂O, respectively. One can easily identify the signals for each proton in PSSO₃Na and TTABr. Figure 2c shows the spectrum of a solution that contained a mixture of PSSO₃Na (1.0 wt %) and TTABr (32.5 mmol L⁻¹) in D₂O at (25.0 ± 0.1) °C. The ¹H NMR spectrum of TTABr was most affected, in particular the protons labeled T₂, T₃, and T₅ in TTABr, which suggests that there is a strong interaction between the anions of PSSO₃⁻ and the cations of TTA⁺ owing to electrostatic and hydrophobic forces.

When the temperature increased from 25 to 90 °C, the phase transition of an aqueous solution that contained PSSO₃Na (1.0 wt %) and TTABr (32.5 mmol L⁻¹) was observed by the naked eye. The clear, colorless solution began to transform into a clear, sky-blue solution at about $T = 65.0$ °C. This observation is consistent with the turbidity heating curve shown in Figure 3. The turbidity increased as the clear, colorless solution transformed into the clear, sky-blue solution. Figure 3 shows that the turbidity began to increase at about 65 °C. As the temperature continued to in-

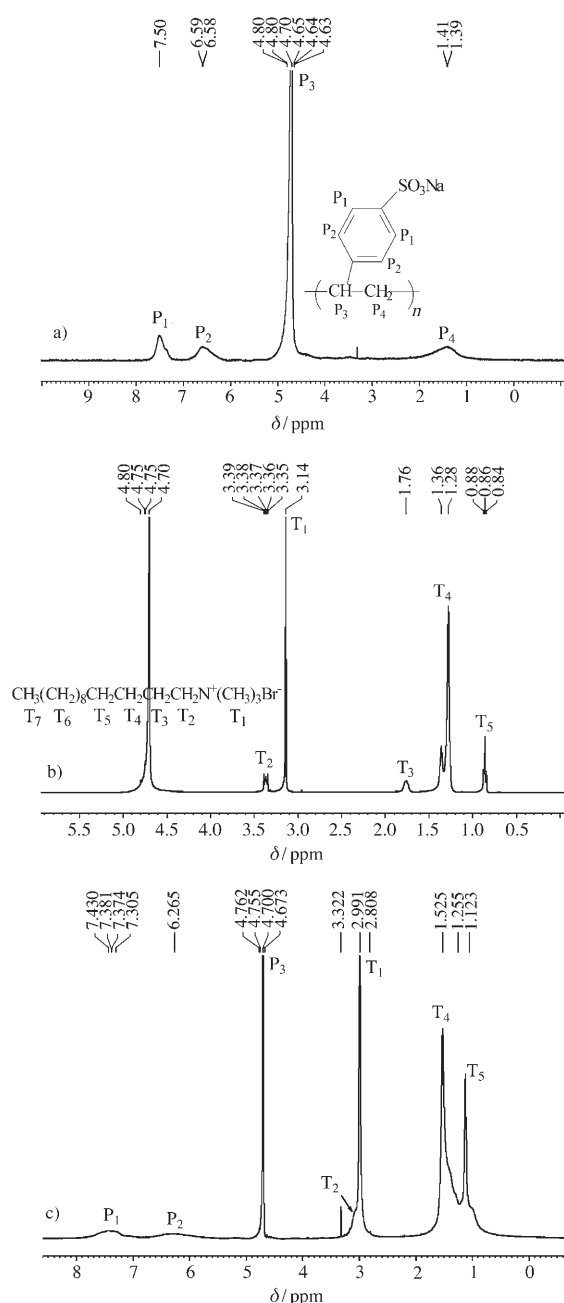


Figure 2. ¹H NMR spectra at (25.0 ± 0.1) °C of a) PSSO₃Na (1.0 wt %), b) TTABr (32.5 mmol L⁻¹), and c) a mixture of PSSO₃Na (1.0 wt %) and TTABr (32.5 mmol L⁻¹) in D₂O.

crease, the clear, sky-blue solution transformed into an opaque, sky-blue solution. The turbidity of the mixture (PSSO₃Na/TTABr, 1.0 wt %:32.5 mmol L⁻¹) increased as the temperature continuously increased from 65 to 90 °C, and after $T = 90$ °C the turbidity of the sample remained almost constant.

It is well known that as the temperature increases the solubility of the ionic surfactant in water increases. Once the temperature reaches a certain value, the solubility increases rapidly; this temperature is called the Kraft point. However, for a nonionic-surfactant solution, as the temperature reach-

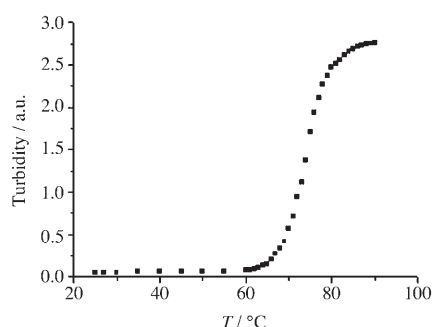


Figure 3. Turbidity change of a solution containing a mixture of PSSO_3Na (1.0 wt %) and TTABr (32.5 mmolL^{-1}) as a function of temperature.

es a certain point the clear solution will suddenly become turbid; this temperature is known as the cloud point because it is the temperature at which clouding occurs. Heat-induced phase separation occurs at the cloud point, which is attributed to dehydration of the hydrophilic groups upon heating. In our study, both PSSO_3Na and TTABr are ionic surfactants, however, mixtures of PSSO_3Na and TTABr possess the properties of nonionic surfactants. When the temperature reaches approximately 60°C , the turbidity of the solution that contains oppositely charged PSSO_3Na and TTABr suddenly increases, which means that the solubility decreases at this temperature. The superstructures formed from oppositely charged PSSO_3Na and TTABr molecules can be used to explain this process.

When the temperature was not continuously increased from 25 to 90°C , but remained at a constant value ($T \geq 65^\circ\text{C}$) for some time, an interesting phase transition was also observed. In our study, we maintained the temperature at $T = (65.0 \pm 0.1)^\circ\text{C}$ and observed that with time the clear, colorless solution of PSSO_3Na (1.0 wt %) and TTABr (32.5 mmolL^{-1}) transformed into a clear, sky-blue solution. Figure 4 shows the change in turbidity at $T = (65.0 \pm 0.1)^\circ\text{C}$ with time. After 3 min, the turbidity of the sample increased slowly and a sky-blue solution ($L\alpha$ phase) was obtained that displayed flow birefringence. The sample consisted of vesicles, the presence of which was demonstrated by means of negative-staining transmission electron microscopy (NS-TEM) and freeze-fracture transmission electron microscopy

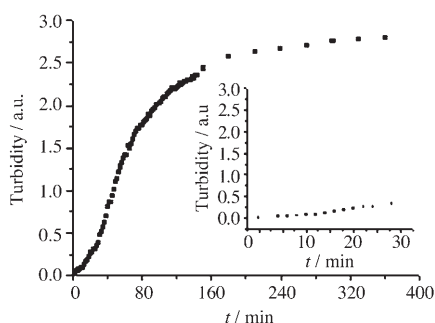


Figure 4. Turbidity change for a solution of PSSO_3Na /TTABr (1.0 wt %: 32.5 mmolL^{-1}) at $T = 65.0 \pm 0.1^\circ\text{C}$. The inset shows the turbidity curve for this system at 65.0°C from 0 to 30 min.

(FF-TEM) (Figure 5). The NS-TEM and FF-TEM images all show that vesicles exist and their diameters are in the range of 20 to 100 nm. Some vesicles agglomerate to form vesicle clusters.

It is obvious that phase transitions lead to the color and

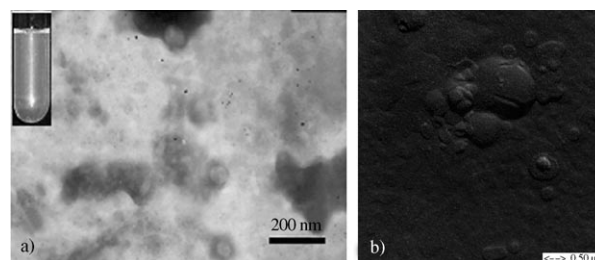


Figure 5. NS-TEM (a) and FF-TEM (b) images for an aqueous solution containing a mixture of PSSO_3Na and TTABr (1.0 wt %: 32.5 mmolL^{-1}) maintained at $T = (65.0 \pm 0.1)^\circ\text{C}$ for 10 to 15 min. The solutions were stained with an aqueous solution of uranyl acetate ($\approx 4 \mu\text{L}$, 2.0 wt %). The inset shows the solution of the sample used.

turbidity changes observed for this system, and also demonstrate changes in the structure of the assemblies. Such temperature-controlled phase transitions from micelles to vesicles in aqueous mixtures of cationic and anionic surfactants have been recently reported.^[4] However, it is the first time that it has been observed in mixtures of oppositely charged polyelectrolytes and surfactants.

The solution that contained PSSO_3Na (1.0 wt %) and TTABr (32.5 mmolL^{-1}) was maintained at $T = (65.0 \pm 0.1)^\circ\text{C}$ to allow for phase equilibration. The flow birefringent, clear, sky-blue solution transformed into an opaque, sky-blue solution in 30 min to 2 h, which suggests the formation of precipitate-like aggregates. Figure 4 shows that the turbidity of the sample rapidly increased during this time period. NS-TEM images of the precipitate-like aggregates (Figure 6) show that they have the morphology of melon seeds. To the best of our knowledge, the time-controlled transition of vesicles into novel superstructures at constant high temperatures has not been presented in the literature to date.

As the length of time that the sample was maintained at higher temperatures increased, for example, more than two hours, the concentration of precipitate present increased. After three hours, flow birefringence was not observed and

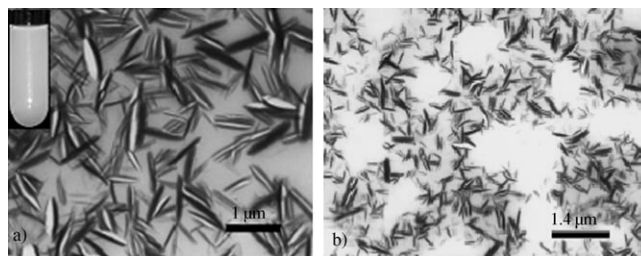


Figure 6. NS-TEM images for a sample of the precipitate-like aggregates obtained from a solution of oppositely charged PSSO_3Na and TTABr maintained at $T = (65.0 \pm 0.1)^\circ\text{C}$ for 50 min. The inset shows the solution of the sample used.

only precipitate existed to totally transform the sample into an opaque, milk-white solution. Figure 4 shows that the turbidity increased slowly and was almost unaltered. The precipitate was observed by means of NS-TEM images. Figure 7 shows that irregular morphologies were observed after the sample solution was maintained at $T=(65.0\pm 0.1)^{\circ}\text{C}$ for 6 h. The complex system forms a distinct bicontinuous structure, which indicates the occurrence of macro-phase separation. Within the bright domains, microaggregates can be observed that might correspond to aggregates of the polar head groups present in PSSO_3Na .

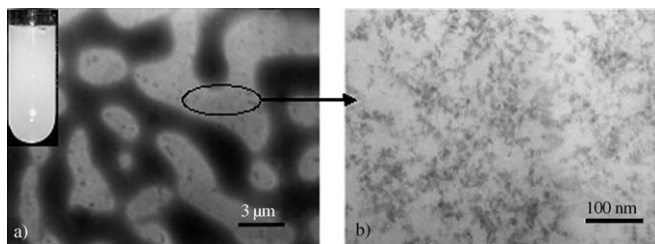


Figure 7. a) TEM images of precipitates obtained from an aqueous mixture of PSSO_3Na and TTABr maintained at $T=(65.0\pm 0.1)^{\circ}\text{C}$ for 6 h, and b) local magnification. The inset shows the solution of the sample used.

A distinct increase in the turbidity of the sample, which suggests the growth of aggregates, was observed both with increasing the temperature from 65 to 90°C (Figure 3), and with increasing the length of time that the solution was maintained at a constant high temperature (Figure 4). Namely, the phase transitions undergo the steps for the formation of vesicles from micelles, then there is the coexistence of vesicles and superstructures that have the morphology of melon seeds, and finally precipitate is formed. It should be noted that these temperature-induced phase transitions are reversible. Reducing the temperature to $25.0\pm 0.1^{\circ}\text{C}$ allows the opaque, milk-white solution to transform into an opaque, sky-blue solution, then into a clear, sky-blue solution and finally into a clear, colorless solution. Lowering the temperature means that the precipitates can dissolve and transfer from precipitate-like aggregates with slight flow birefringence to a flow birefringent L_{α} phase and finally to the clear L_1 phase. These processes need several days to complete. Several heating and cooling cycles were performed on the same sample and the results that were obtained are reproducible, which indicates the reversibility of the phase transitions.

Conclusions

In conclusion, an aqueous solution containing a mixture of PSSO_3Na (1.0 wt %) and TTABr ($30.0\text{--}34.0\text{ mmolL}^{-1}$) undergoes apparent transitions from a clear, colorless solution to a clear, sky-blue solution, then to an opaque sky-blue solution, and finally to an opaque, milk-white solution as the temperature increases. These transformations are consistent

with phase transitions from micelles to vesicles, then the coexistence of vesicles and aggregates that have the morphology of melon seeds, and finally to precipitates. These phase transitions can be obtained either through maintaining the sample at a high temperature for longer time periods ($T\geq 65^{\circ}\text{C}$) or through increasing the temperature from room temperature to higher temperatures ($T>65^{\circ}\text{C}$). The phase transitions are reversible. Although the phase transition in cationic or anionic surfactant solutions (i.e., the phase transition from micelles to vesicles)^[8–13] was induced through heating the sample, complicated phase transitions in the present system, which is composed of oppositely charged PSSO_3Na and TTABr molecules, have been observed for the first time. The phase-transition mechanism for the transformation from primary aggregates to superstructures by using temperature control is more complex and not completely clear. Additionally, PSSO_3Na and TTABr are ionic surfactants, but the phenomena observed is different from that conventionally observed. Elucidation of the mechanism should provide new understanding for surfactant sciences, in particular for self-assembled amphiphilic systems.

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