Micelle to Vesicle Transition

Temperature-Induced Micelle to Vesicle Transition in the Sodium Dodecylsulfate/Dodecyltriethylammonium Bromide System[**]

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Amphiphilic molecules have the ability to form organized assemblies such as micelles, vesicles, and lamellar structures in solution. Different kinds of assemblies can be transformed by the change of various environmental factors.[1] Temperature often plays an important role in such transitions.[2] The

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transition from an ordered state to a disordered one[3] or from a higher ordered state to a lower ordered one (such as the transition from a vesicle to a micelle[4]) on increasing the temperature usually occurs among organized assemblies. However, studies of the reverse temperature-induced transitions, such as micelle to vesicle transition (MVT), are so far rare. Herein, we report for the first time a temperature-induced MVT in a cationic–anionic surfactant system.

The sodium dodecylsulfate (SDS)/dodecyltriethylammonium bromide (DEAB) system was prepared in a molar ratio of 2:1 and a total concentration (C_{total}) of 10 mM. The results of the turbidity measurements are shown in Figure 1 a. A clear increase in turbidity was observed as the temperature increased from 30 to 50 °C, which suggests the growth of aggregates in the system. No phase separation or precipitate was observed during the transition, which is different from the "cloud point" phenomena seen in some ionic surfactant systems.[5]

Dynamic light scattering (DLS) studies, a freeze fracture technique with observation by electron microscopy (FF-EM), and rheology measurements were used to investigate the temperature-induced transition in the system. The aggregate has an average hydrodynamic radius ($\langle R_h \rangle$) of 25 nm at 20 °C (Figure 2 a). A steady flow curve (Figure 3) revealed the non-Newtonian nature of the system and thus indicated the existence of asymmetric aggregates. A remarkable shear-thickening feature was also evident in the flow curve. It has been well documented[6] that the growth or flow alignment of cylindrical micelles was responsible for the shear-thickening behavior in dilute surfactant solutions. However, a few small spherical vesicles were also observed by FF-EM (Figure 4 a). Thus, we can conclude that cylindrical micelles are the major aggregates which coexist with a few small spherical vesicles in the system. Similar results were obtained at 25 °C from DLS (Figure 2 b) and rheology curves, which indicate there was no apparent change between 20 and 25 °C.

However, the situation became different as the temperature increased to 30 °C. A DLS plot (Figure 2 c) showed that the peak corresponding to the small aggregates ($R_h \sim 25$ nm) shrank relative to that at 25 °C, while another peak appeared ($R_h \sim 100$ nm). The polydispersity index (PI, calculated by the Cumulant method) grew from 0.282 (25 °C) to 0.339 (30 °C), which was indicative of the increase in the vesicle/micelle ratio in the system.[7] Vesicles with a diameter of 150–200 nm were observed by FF-TEM (Figure 4 b), which coincides with the newly appeared peak in the DLS plot. Moreover, there

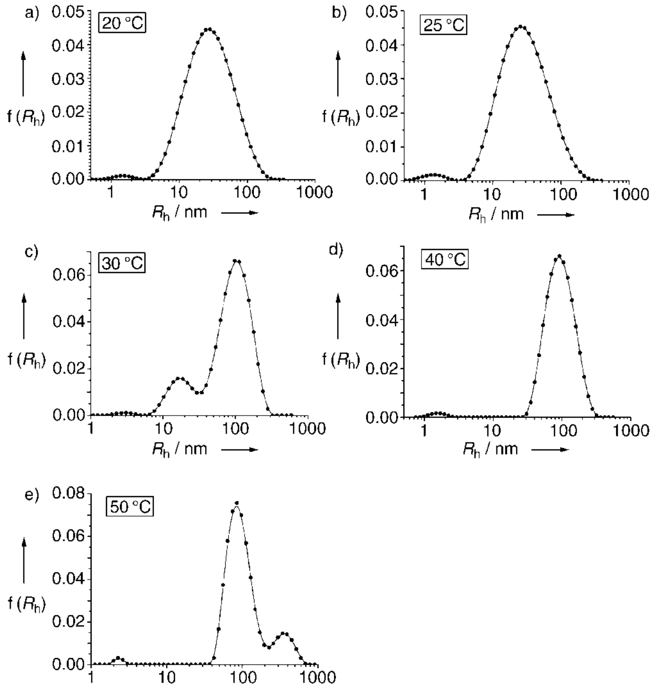

Figure 2. Hydrodynamic radius (R_h) distributions of SDS/DEAB (2:1, C_{total} = 10 mM) at 20 °C (a), 25 °C (b), 30 °C (c), 40 °C (d), and 50 °C (e) calculated by the Contin method.

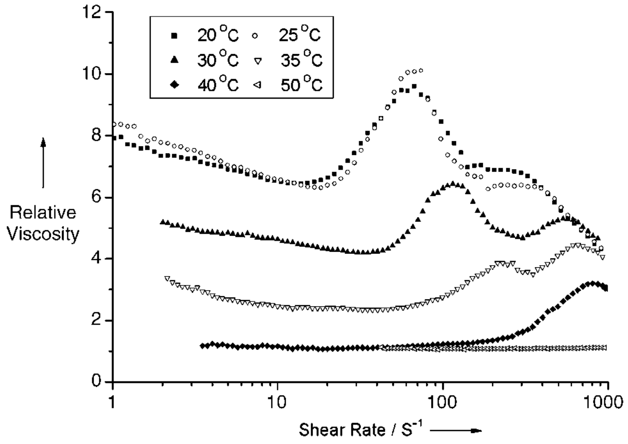

Figure 3. Steady flow curves as a function of temperature in SDS/DEAB (2:1, C_{total} = 10 mM).

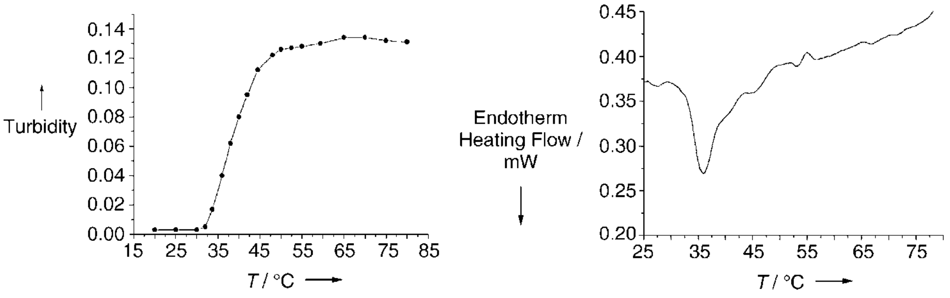

Figure 1. Turbidity curve (a) and DSC heating curve (b) of the SDS/DEAB (2:1, C_{total} = 10 mM) system as a function of temperature.

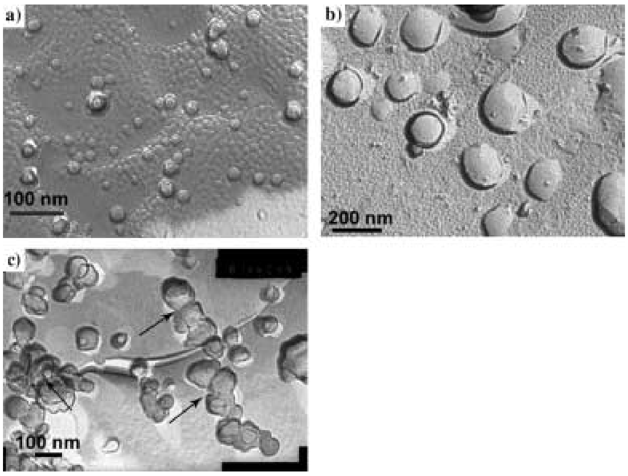

Figure 4. Vesicles of the system SDS/DEAB (2:1, $C_{total} = 10$ mM) observed by FF-EM at 20 °C (a), 30 °C (b), and 50 °C (c). Solid arrows show the aggregation of vesicles.

was a dramatic decrease in the relative viscosity at low shear rate. All these results confirm that the increase in turbidity with increasing temperature is actually caused by the transition from cylindrical micelles to vesicles in the system.

The MVT process continued as the temperature was further increased. At 40 °C, the system showed approximate Newtonian characteristics under low shear rate despite shear-thickening behavior still being present at a high shear rate. This result suggests that the aggregates in solution become more symmetrical. In the DLS plot, the R_h peak at approximately 25 nm assigned to cylindrical micelles almost disappeared, to leave the R_h peak of about 100 nm assigned to vesicles (Figure 2 d). The low PI value (0.195) also indicates that vesicles are the dominating aggregates in the system. Further heating to 50 °C resulted in the system becoming a completely Newtonian fluid (Figure 3) and its relative viscosity was approximately unity ($\eta_r = 1.08$). Large vesicles still existed in the system (Figure 4 c). Thus, it can be concluded that the cylindrical micelles were almost completely transformed into vesicles at this temperature. Consequently, the turbidity remained nearly constant upon further heating. However, another peak emerged with an R_h value of 200–300 nm in the DLS plot (Figure 2 e), and the PI value correspondingly increased to 0.21. The formation of these larger aggregates may be attributed to the aggregation of the vesicles (Figure 4 c).

The transition between the micelle and the vesicle is often accompanied by a heat effect.[8,9] Therefore, DSC measurements were employed to monitor the temperature-dependent transition. An endothermic peak can clearly be observed in the heating curve (Figure 1 b). Compared with the turbidity curve, this peak appeared during the interval of transition (from ca. 30 °C to ca. 50 °C). It is possibly a result of the positive transfer enthalpy of micelle to vesicle transition, which was elucidated to extensively in another study.[9] The result of the DSC studies also provides strong support for our conclusion.

Several heating–cooling cycles were performed on the same sample and the results obtained were reproducible, which indicates the reversibility of the transition. Such a transition was also remarkably influenced by the molar ratio of the anionic/cationic surfactants and the total surfactant concentration.

In summary, cylindrical micelle to vesicle transition upon an increase in the temperature was demonstrated in the system of SDS/DEAB (2:1, $C_{total} = 10$ mM). A clear transition occurred between 30 and 50 °C. Although temperature-induced MVT was previously reported in some lipid/surfactant,[9] non-ionic surfactant,[10] and ionic surfactant/cosurfactant[11] systems, the transition in our case can not be explained simply with the interpretations for the above systems, and seems to come from a more complex origin. However, the temperature-dependent interaction of the oppositely charged surfactant molecules should play a key role in this case.

Experimental Section

Materials: SDS was bought from ACROS ORGANICS Co. (99% purity). DEAB was synthesized from dodecyl bromide and triethylamine. The purity of all the surfactants was examined and no surface tension minimum was found in the surface tension curve.

Turbidity measurements were carried out using a Shimadzu UV-250 spectrophotometer at 514.5 nm.

DLS measurements were performed with a spectrometer (ALV-5000/E/WIN Multiple Tau Digital Correlator) and a Spectra-Physics 2017 200 mW Ar laser (514.5 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed by using the methods of Contin and Cumulant.

Samples for electron microscopy were prepared by freeze-fracture replication according to standard techniques with a high vacuum freeze-etching system (FED.B-JEE-4X). Replicas were observed with a JEM-100CX electron microscope.

The rhoelogical properties of the samples were measured with a ThermoHaake RS300 rheometer. A double gap cylinder sensor system was used with an outside gap of 0.30 mm and an inside gap of 0.25 mm.

DSC measurements were carried out 1 °C min^{-1} using Micro DCS III (Setaram-France) instrument.

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