

APPLICATION NOTE



Measuring the Size of Self-Assembled Surfactant Micelles at Different Temperatures and Concentrations

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Introduction

Surfactants are amphiphilic molecules containing hydrophilic part and hydrophobic part. When surfactants are dissolved into water, they orient themselves at the air-water interface so that the hydrophilic part is in water and the hydrophobic part in the air. When the surfactant concentration is higher than the critical micelle concentration (CMC), the surfactant molecules will be regularly arranged on the liquid surface or form micelles through self-assembly behavior. Note that the change of ambient temperature and surfactant concentration will result in different phase behaviors of the micelles and consequently different sizes and morphologies. There are many types of surfactant molecules, which can be divided into non-ionic surfactants such as the CmEn series, ionic surfactants such as SDS, and copolymer surfactants. The phase behavior of a particular surfactant is determined by its specific type or chemical composition. Surfactants have a wide application in various fields including chemistry, biology, pharmaceuticals, etc.

In this application note, a non-ionic surfactant micelle Tween 20 and an ionic surfactant micelle SDS were studied by investigating their particle sizes and the effect of temperature on their phase behaviors through dynamic light scattering (DLS) technology.



Theory and Instrumentation

DLS measures the intensity fluctuations of the sample due to Brownian motions of particles. The diffusion coefficient D is obtained and related to the particle size, i.e., the hydrodynamic diameter DH, by the Stokes-Einstein equation.

$$D = \frac{k_B T}{3\pi \eta D_H}$$

Where kB is the Boltzmann constant, T is the temperature, and η is the dispersant viscosity.

In this study, the surfactant samples were characterized by the BeNano 90 Zeta (Bettersize Instruments Ltd.), which adopts a He-Ne laser with the wavelength of 633nm and the power of 10mW. In addition, in the BeNano 90 Zeta, single-model optical fibers are used for signal transmission in order to maximize the signal-noise ratio; high-speed correlators are utilized such as that the fast-decay correlation functions for small particles can be calculated effectively.

Sample	Concentration Dispersant		
Tween 20	10 mg/mL	Water	
Tween 20	25 mg/mL	Water	
Tween 20	50 mg/mL	Water	
SDS	25 mg/mL	Water	
SDS	50 mg/mL	Water	

Table 1. Sample Information

Experiment

Two surfactant suspensions were prepared at different concentrations as shown in Table 1.

The measurement temperature was set to be $25 \text{ C} \pm 0.1 \text{ C}$ through the built-in temperature control system of the BeNano 90 Zeta. Since the surfactant molecules were very small and the scattering intensity was extremely weak, the presence of impurities, such as dust, would have a great impact on the measurement results. Therefore, the samples were filtrated by a 220nm filter before the measurement. Each sample was measured at least three times to ensure repeatability of the results.

Results and Discussion

The correlation functions were calculated through the scattered signals of samples.

According to the correlation functions shown above, all the samples decayed extremely fast, due to the rapid Brownian motions of small particles. As shown in Figure 1, the signal-noise ratios of correlation functions were good, and the decay rates increased with the temperature, since the micelles diffused faster at higher temperature. The powerful calculation capability of the BeNano 90 Zeta enables sufficient points on correlation functions for small particles.

Figure 2 and Figure 3 illustrate the correlation functions of 25mg/mL and 50mg/mL Tween 20 micelles obtained by multiple measurements, respectively. It can be seen that the repeatability of measurements was very good even for several-nanometer particles with extremely weak scattering intensity, indicating the high sensitivity and stability of the BeNano 90 Zeta.



Figure 1. Correlation functions of 10mg/mL Tween 20 at temperatures ranging from 5 °C to 65 °C



Figure 2. The overlap of correlation function of 25mg/mL Tween 20 at 25 $^\circ\!\mathrm{C}$



Figure 3. The overlap of correlation function of 50mg/mL Tween 20 at 25 $^\circ\!\mathrm{C}$



Figure 4. The overlap of correlation function of 25mg/mL SDS self-assembled micelle



Figure 5. The overlap of correlation function of 50mg/mL SDS self-assembled micelle



Figure 6. Particle size distributions of 10mg/mL Tween 20 at the temperature from 5 \odot to 65 \odot



Figure 7. Particle size distributions of 25mg/mL SDS micelle at 25 $^\circ\!\mathrm{C}$



Figure 8. Particle size distributions of 50mg/mL SDS micelle at 25 °C

Figure 4 and 5 above show the correlation functions of 25 and 50 mg/mL micelles within different sub runs. The almost perfect overlaps of correlation functions suggest that the algorithm in the correlator of the BeNano 90 Zeta has great sensitivity and accuracy. In Figure 6, particle size distributions of 10 mg/mL Tween-20 at temperatures varying from 5°C to 65°C are presented. It can be seen that the particle sizes of Tween-20 were barely changing as the temperatures varied, indicating a good thermal stability. Figures 7 and 8 are the particle size distributions of SDS micelle at 25°C with a 25 and 50 mg/mL concentration, respectively.

Sample Concentrations	Temperature (°C)	Z-ave (nm)	
10 mg/mL Tween	5	7.12±0.41	
10 mg/mL Tween	10	8.11±0.17	
10 mg/mL Tween	15	8.14±0.12	
10 mg/mL Tween	20	7.86±0.01	
10 mg/mL Tween	25	7.56±0.07	
10 mg/mL Tween	35	7.16±0.25	
10 mg/mL Tween	45	6.96±0.08	
10 mg/mL Tween	55	6.88±0.15	
10 mg/mL Tween	65	7.24±0.06	
25 mg/mL Tween	25	7.41±0.10	
50 mg/mL Tween	25	7.30±0.14	
25 mg/mL SDS	25	53.03±7.23	
50 mg/mL SDS	25	2.21±0.1	

Tabl	e 2.	Z-average	sizes o	f micell	e samples
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As seen in Table 2, the Z-ave values of micelles formed by Tween 20 surfactant under different conditions was relatively stable, fluctuating between 7.3nm and 7.6nm in the concentration range from 10mg/mL to 50 mg/mL at 25 \degree . When the concentration was 10mg/mL, the Z-ave of Tween 20 sample was between 6.8nm and 8.1nm at the temperature ranging from 25 \degree to 65 \degree .

As we know, for SDS surfactant micelles, the particle size highly depends on its concentration. At a concentration of 25 mg/ mL, in addition to the formation of several nanometer-sized micelles, large aggregates of several hundred nanometers also formed. When the concentration increased to 50mg/mL, the amount of large micelle aggregates decreased significantly.

Conclusion

The particle sizes of self-assembled micelles (ionic and non-ionic) had been characterized successfully by the DLS technology of the BeNano 90 Zeta. The built-in temperature control unit in the BeNano 90 Zeta allows the thermal stability analysis on particle sizes by controlling the sample temperature to the desired value with the precision of $\pm 0.1^{\circ}$ C.



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