

Time-Resolved SAXS Studies of Mixture of Anionic and Cationic Surfactants

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Time-resolved SAXS spectra emerged from the nano-structure formed after mixing of cationic dodecyltrimethylammonium chloride (DTAC) and anionic sodium dodecylsulfate (SDS) solutions were investigated. The catanionics with equal length tails are known to exhibit a lamella structure at equilibrium. In the present investigation, however, we found that a vesicle structure formed immediately after mixing ($t=0.038$ sec) and a lamella structure grew later with time elapsed after mixing. It is found that the peak intensity identified with vesicle exponentially decays with time. The decay time τ increases with NaCl concentration of the mixture. This result indicates that the vesicles are stabilized by the shielding of the electrostatic interaction due to the added salt. On the other hand, the peak intensity identified with lamella is described by a power law of time and the exponent of the power function is found to increase with NaCl concentration.

Key words: Single-tailed surfactant, Vesicle, Lamella, Small angle X-ray scattering, Stopped-flow

1. INTRODUCTION

Unilamellar vesicles consisting of surfactant molecules have great potential for applications such as catalysis and microencapsulation for drug delivery. Vesicle formation as the equilibrium structure, however, has been considered to be impossible without mechanical input (sonication or pressure filtration) or elaborate chemical treatments (detergent dialysis or reverse-phase evaporation) [1-2]. Recently, it has been found that aqueous mixtures of anionic and cationic surfactants form vesicles spontaneously [3-5]. Studies have been rarely reported on the temporal evolution of vesicle formation [6-7]. Understanding the dynamical behavior of microstructures formed in the surfactant solution is a key to produce spontaneous and stable vesicles. In the present paper, we will report time re-solved small-angle X-ray scattering (SAXS) spectra obtained for the rapidly mixed anionic sodium dodecylsulfate (SDS) and cationic dodecyltrimethylammonium chloride (DTAC) solutions with a stopped-flow apparatus. The equimolar cationic and anionic surfactants, catanionics with equal length tails are known to produce a lamella structure at equilibrium [8]. The present experiments, however, demonstrated that the vesicles formed just after mixing and annihilated, and that the lamella structure grew with an elapsing time to reach the equilibrium. The annihilation time of vesicle and the growth rate of lamella structure depended on the salt concentration added to the solution.

2. EXPERIMENTAL PROCEDURES

DTAC (Tokyo Chemical Industry, Tokyo) and SDS (Katayama Chemical Industry, Osaka) were recrystallized from ethanol/acetone and used. NaCl (Nakalai tesque, Kyoto) was used as received.

Time-resolved SAXS experiments were carried out with SAXS spectrometer of BL45XU (RIKEN Beam-line) installed at SPring8, Hyogo, Japan.

Equal amounts (typically 0.5mL) of DTAC and SDS aqueous solutions were mixed within 5 ms by using the stopped-flow apparatus (Unisoku Co. Ltd., Japan) and the data acquisition of time-resolved SAXS spectra was hardware synchronized with the mixing sequence of the stopped-flow apparatus ($t=0$). The experiments were carried out for the 50 and 100 mM surfactant solutions with various NaCl concentrations (0, 350, 550, 750 mM).

3. RESULTS AND DISCUSSION

3.1 Nano-structure after mixing of anionic and cationic surfactants

The stopped-flow mixing of equal amounts of aqueous 50 mM surfactants and 350 mM NaCl solutions was carried out. The time profile of SAXS spectra of the mixture after mixing is shown in Fig. 1. A transient broad peak at $q=0.44$ nm⁻¹ and a sharp but weak peak at $q=1.87$ nm⁻¹ appear immediately after mixing ($t=0.038$ sec) as shown in Fig. 1. The former peak vanishes at $t=22.647$ sec while the intensity of the latter increases with a time elapsed after mixing. The characteristic lengths of the periodic structures estimated from these scattering peaks are about 14 nm and 3.4 nm respectively. The lamella structure with 3.4 nm period is consistent with the chain lengths of SDS and DTAC being about 1.5 nm. The characteristic length of 14 nm is considered to be too large for the lamella or the micelle structure. Figure 2 shows the magnified spectra of Fig. 1. The scattering spectra can be fitted well with the following function [6].

$$I(q) = N \int_0^\infty f(r)P(q,r)dr, \quad (1)$$

where $P(q, r)$ is a form factor of polydisperse shells, N is the number density of vesicles, and $f(r)$ is the Schulz size distribution as follows;

$$f(r) = \left(\frac{z+1}{R_m}\right)^{z+1} \frac{r^z}{\Gamma(z+1)} \exp\left(-\frac{z+1}{R_m}r\right) \quad (2)$$

Here R_m is the mean radius. The polydispersity is characterized by $z+1=1/p^2$, where p is the polydispersity index [$p = (\langle R^2 \rangle / R_m^2) - 1$]. $P(r)$ is given by

$$P(q) = 16\pi^2 (\rho_A - \rho_S)^2 \{R_2^3 f_0(qR_2) - R_1^3 f_0(qR_1)\}^2, \quad (3)$$

where $f_0 = (\sin x - x \cos x)/x^3$ and ρ_A and ρ_S are the scattering length densities for the bilayer and the solvent, respectively. The outer radius R_2 was chosen to be $R_1 + 1.7$ nm being consistent with the chain length of surfactants. The first peak at 0.44 nm^{-1} is fitted well with the calculated solid line. The fitting to the weak second peak at $q=0.94 \text{ nm}^{-1}$ is poor, indicating that the nanostructure inside the shell is not well described by the present model. There might be some sophisticated structure related to the micelle. From the fit, the mean radius R_m and the polydispersity index p were estimated as 8.5 nm and 0.17, respectively. Therefore, it can be inferred that broad peak can be identified as a spherical vesicle. From the present observation, we can say that the vesicle formation is achieved within 30 ms after mixing. The collision of anionic and cationic micelles due to the strong electrostatic attraction yields the mixed micelle, which might be a curved disk because of the asymmetric distribution of cationic and anionic surfactant molecules due to the aggregation number difference between them. The curved disks fuse to form the vesicle, which contains the micelle with smaller aggregation number. The attraction between the vesicle shell and the micelle drives the fusion of them to disintegrate the micelle and the vesicle. This process is driven by the electrostatic interaction, which might be controlled by adding the salt to the solution.

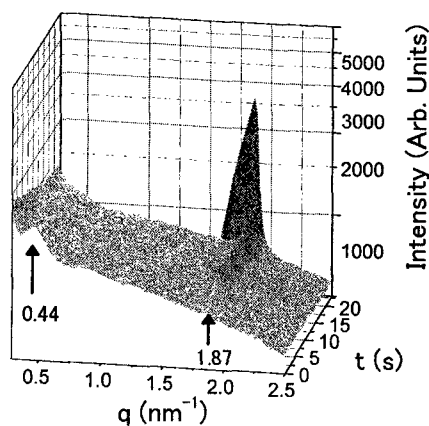


Figure 1. 3D plot of time-resolved SAXS spectra after mixing DTAC (50 mM)/ NaCl (350 mM) and SDS (50 mM)/ NaCl (350 mM).

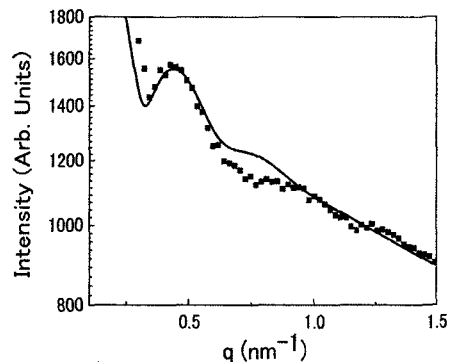


Figure 2. The magnified spectra of Fig.1 ($t=0.115$ s). A bold solid line shows the calculated spectrum using a model of polydisperse shells.

3.2 Salt effect to formation of nano-structures

The salt concentration of solution was changed from 0 mM to 750 mM in order to examine the kinetic process driven by the electrostatic interaction. Figure 3 shows the salt concentration dependence of time profiles of the vesicle peak intensity for the mixture of 50 mM DTAC and 50 mM SDS. Upper and lower figures show time profiles at a long time and a short time respectively. Solid lines in Fig. 3 represent curves of exponential functions $I_v(t) = C_1 \exp(-t/\tau)$ best fitted to the experiment, where $I_v(t)$ is the vesicle intensity and τ is a decay time. It can be concluded from the fitting that the vesicle intensity exponentially decays with time. The fitted τ is tabulated in Table 1. The τ increases with NaCl concentration, C_s of the mixture. From this we can infer that the vesicles are stabilized by the shielding of the electrostatic attraction between the vesicle shell and the micelle inside it. We also examined the mixture of aqueous solution of 100 mM DTAC and 100 mM SDS with various C_s . The obtained results are also tabulated in Table 1. The τ for the mixture 100 mM DTAC with 100 mM SDS increases with C_s , which is similar to the case of 50 mM DTAC and 50 mM SDS. It is obvious from Tables 1 that the annihilation time τ of vesicle in the 100 mM cationic solution is significantly shorter than that in the 50 mM anionic solution. The scattering vector of vesicle peak, q_v for the former is smaller than that for the latter as shown in Tables 1. This indicates the vesicle size increases with the surfactant concentration. The large vesicles formed in the solution at the high surfactant concentration are more unstable as long as the C_s is unvarying.

Figure 4 shows the salt concentration dependence of time profiles of the lamella intensity for the mixture of 50 mM DTAC and 50 mM SDS. Upper and lower figures show time profiles at a long time and a short time respectively. There exist fast and slow processes in the lamella intensity growth. The intensity is normalized by the intensity at the time when the growth rate sharply changes and plotted in Fig. 4. The fast growth is interesting since it occurs at the time during which the vesicles annihilate. Solid lines in Fig. 4 represent the curves of $I_l(t) = C_2 t^\alpha$ best fitted to the experiment, where $I_l(t)$ is the lamella intensity. As shown in the short time profile in Fig. 4, the time dependence of the lamella intensity is well described by a power law of time and it

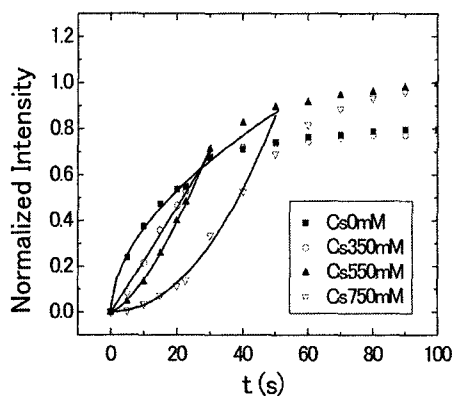
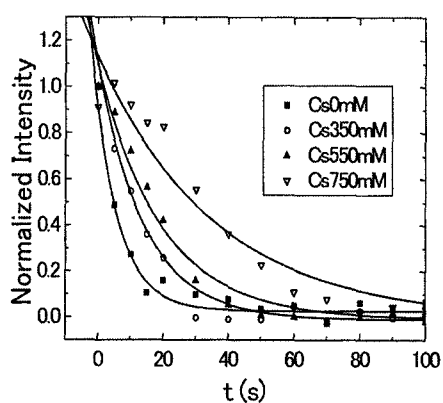
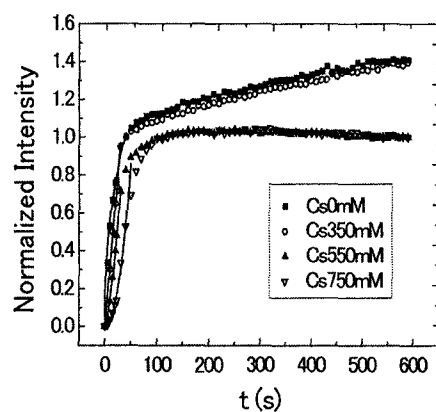
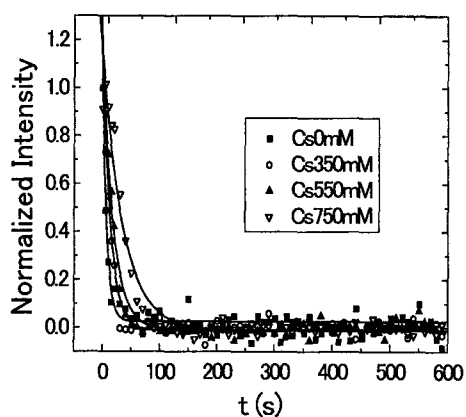


Figure 3. Time profiles of the normalized vesicle intensity for mixture of 50 mM DTAC and 50 mM SDS. Upper and lower figures, respectively, show a long time profile and a short time profile. Solid lines show the curves of exponential functions best fitted to the experiment.

Figure 4. Time profiles of the normalized lamella intensity for mixture of 50 mM DTAC and 50 mM SDS. Upper and lower figures, respectively, show a long time profile and a short time profile. Solid lines show the curves of power laws best fitted to the experiment.

TABLE 1. Parameters characterizing the kinetics of vesicle annihilation for the mixture of DTAC and SDS.

NaCl (mM)	τ (s)		q_v (nm ⁻¹)	
	50 mM DTAC/ 50 mM SDS	100 mM DTAC/ 100 mM SDS	50 mM DTAC/ 50 mM SDS	100 mM DTAC/ 100 mM SDS
0	7.78 ± 0.18	3.79 ± 0.08	0.45	0.41
350	14.28 ± 0.19	5.5 ± 0.07	0.44	0.41
550	19.50 ± 1.00	7.76 ± 0.07	0.45	0.41
750	36.27 ± 2.26	21.39 ± 1.72	0.40	0.36

TABLE 2. Parameters characterizing the kinetics of lamella growth for the mixture of DTAC and SDS.

NaCl (mM)	α		q_l (nm ⁻¹)	
	50 mM DTAC/ 50 mM SDS	100 mM DTAC/ 100 mM SDS	50 mM DTAC/ 50 mM SDS	100 mM DTAC/ 100 mM SDS
0	0.50 ± 0.03	0.74 ± 0.02	1.87	1.87
350	1.03 ± 0.04	0.94 ± 0.02	1.87	1.87
550	1.71 ± 0.01	1.19 ± 0.02	1.87	1.87
750	1.96 ± 0.01	2.30 ± 0.02	1.87	1.87

changes from a hyperbolic curve to a quadratic curve with increasing Cs. The fitted α and the scattering vector of lamellae peak, q_1 are tabulated in Table 2. The crystalline nucleation and growth processes have been often theoretically explained by a power law of time [10]. According to the theory developed by Avrami, the α -value is a convenient index of growth types [10];

$3 \leq \alpha \leq 4$ for polyhedral growth.

$2 \leq \alpha \leq 3$ for plate-like growth.

$1 \leq \alpha \leq 2$ for lineal growth. (4)

The growing process of lamellae in the present experiment can be identified as plate-like or lineal growth from the α -values shown by Table 2. In the case of the mixture of aqueous solution of 100 mM DTAC and 100 mM SDS with NaCl, the similar time dependence of the lamella intensity was observed. The fitted α and the scattering vector of lamellae peak, q_1 are also tabulated in Table 2. The plate-like or lineal growth of the lamella in the 100 mM surfactant solutions can be also inferred from the α -values shown by Table 2. The q_1 is constant regardless of Cs or surfactant concentration while the q_0 not. It should be mentioned that the slow processes of lamella intensities at the low Cs (0 mM and 350 mM) are different from those at the high Cs (550 mM and 750 mM).

As shown in Figs. 3 and 4, the decays of the vesicle intensity and the growth rates of lamella intensity are the slower at the higher Cs. The coupling of vesicle annihilation with lamella formation is likely to exist, although the behavior of vesicle annihilation and lamella formation are described by different functions. Further investigation needs to clarify it.

4 CONCLUSION

Time-resolved SAXS spectra emerged from the nano-structure formed after mixing of anionic and cationic surfactants were investigated. It is surprising that the vesicles form within 30 ms after mixing and annihilate at an elapsed time. The vesicle intensity is found to decay exponentially and the peak assigned to the lamella structure is found to grow with the power law of time. The kinetic process of these nano-structure formations was changed with salt concentration Cs. The decay time of vesicles and the exponent of the power function of time, α increases with Cs. It is considered that the lifetime of vesicle is prolonged by the shielding of the electrostatic interaction among the ionic surfactant molecules. From the observed α -values, the growing process of the lamellae is inferred as plate-like growth in high Cs and lineal growth in low Cs.

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