Time-Resolved SAXS Spectra after rapidly Mixing Anionic and Cationic Surfactants

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Unilamellar vesicles consists of a surfactant bilayer have great potential for applications such as catalysis and microencapsulation for drug delivery. Vesicle formation as the equilibrium structure in a simple water-surfactant system has been believed to be difficult for long period. The well-controlled vesicle has been recently found to be formed with pseudo-double-chained surfactants such as mixtures of cationic and anionic surfactants, catanionics, which show a rich phase behavior; liquid-crystal, vesicle and micelle phases depending on the tail length of the surfactants. The catanionics with equal length tails are known exhibit a lamella structure at equilibrium. In the present investigation, however, we found the vesicle-like structure in the time-resolved SAXS spectra of the rapidly mixing cationic dodecyltrimethylammonium chloride (DTAC) and anionic sodiumdodecylsulfate (SDS) solutions.

DTAC and SDS were recrystalized from ethanol-/acetone and used. Time-resolved SAXS experiments were carried out with SAXS spectrometer of BL45XU (RIKEN Beamline) installed at SPring8, Hyogo, Japan. Small amounts (typically 0.5mL) of 50 mM DTAC and 50 mM SDS aqueous salt solutions (0, 50, 150, 350 mM NaCl) were mixed within a dead time (=5 ms) by using a stopped-flow apparatus and the data acquisition was hardware synchronized with the mixing sequence of the stopped-flow apparatus (t=0).

Figure 1 shows the time evolution of scattering spectra for the mixture of DTAC (50 mM)/NaCl (350 mM) and SDS (50 mM)/NaCl (350 mM) solutions. Immediately after mixing (t=0.03 sec), a transient broad peak at $q = 0.478\ nm^{-1}$ and a sharp but weak peak at $q = 1.920\ nm^{-1}$ appear. The former peak vanishes at t=30 sec while the intensity of the latter grows with time elapsed after mixing. The characteristic lengths of the periodic structures emerging these scattering peaks are about 13 nm and 3.3 nm. The chain lengths of SDS and DTAC being about 1.5 nm can lead to the lamella structure with 3.3 nm period. It can be inferred from a seemingly sinusoidal SAXS spectrum shown in Fig. 1 that the periodic structure with 13 nm length is a vesicle. The second peak weakly recognized at $q = 0.876\ nm^{-1}$ (inset to Fig. 1) also suggests the existence of vesicles.

It is found that the vesicle peak intensity at $q = 0.478\ nm^{-1}$ exponentially decays with time. The decay time, τ increases with NaCl concentration of the mixture (Table 1). The peak intensity is proportional to a population of the vesicle. The NaCl concentration dependence mentioned above indicates that the vesicles are stabilized by the shielding of the electrostatic interaction due to the added salt.

On the other hand, the growing peak intensity at $q = 1.920\ nm^{-1}$, $I(t)_l$, is described by such a power law as $I(t)_l = Ct^{\alpha}$. Although the α-value increases with NaCl concentration from 0.8 at 0 mM NaCl to 1.2 at 350 mM NaCl, we can say that the lamella population proportional to the peak intensity increases linearly with t.

As shown in Table 1, the vesicle peak position q_v moves to high q with increase of NaCl concentration, while the lamella peak position q_l does not change. This indicates that the vesicle size is affected by the electrostatic interaction.

Table 1: q_v, q_l and fitted τ

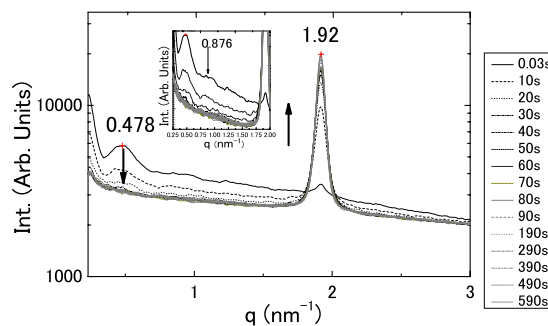| NaCl (mM)	$\tau(s)$	$q_v(nm^{-1})$	$q_l(nm^{-1})$
0	6.5 ± 0.4	0.397	1.920
50	6.1 ± 0.5	0.438	1.920
150	7.8 ± 0.5	0.442	1.920
350	11.5 ± 0.7	0.487	1.920

Figure 1: Time profile of the SAXS spectra for equimolar mixture of DTAC and SDS at 350 mM NaCl. The inset shows an enlarged view of the second peak due to the vesicle.