【Electronic Supplementary Information】

Tuning of the aggregation number of platonic micelle with binary mixture of calix[4]arene surfactants

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EXPERIMENTAL SECTION

Critical Micelle Concentration (CMC) Measurements. The concentration of an aqueous micelle solutions were adjusted to 10 mM, and the solution was diluted with 50 mM aqueous NaCl. The pH of the solution was controlled with 1 M HCl, Tris-HCl buffer, and 1 M NaOH aqueous solutions. Sodium 8-anilino-1-naphthalenesulfonic acid (ANS) was used as a fluorescence probe. The stock solution of ANS was prepared at a concentration of 0.1 mM in water and was then diluted to 10 μM in each solution. The fluorescence measurements were carried out with a fluorescence spectrometer (Jasco FP-6600). ANS was excited at 350 nm, and the emission spectra were recorded at 400−700 nm. The scan speed was 240 nm min^{-1}. The fluorescence intensity of ANS sensitively reflects the polarity of its environment; therefore, the CMC can be determined from a plot of the fluorescence intensity vs the micelle concentration.

Small Angle X-ray Scattering (SAXS) Measurements. Small-angle X-ray scattering (SAXS) measurements were carried out at the BL-40B2 beamline of the SPring-8 facility (Hyogo Prefecture, Japan). A 30 × 30 cm^2 imaging plate (Rigaku R-AXIS VII) detector was placed 1 m from the sample. The wavelength of the incident beam (λ) was adjusted to 0.10 nm. This setup provided a q range of 0.20−4 nm^{-1}, where q is the magnitude of the scattering vector, defined as $q = 4\pi \sin\theta/\lambda$, with a scattering angle of 2θ. The X-ray transmittance of the samples was determined by using ion chambers located in front of and behind the sample.

Determination of Micellar Molar Mass by SAXS. The weight average molar mass of the micelles can be given by the following equation ;

$$M_w = I(0)\{N_A c(\Delta\rho\bar{v})^2\}$$

where Mw is the weight-average molar mass, c is the concentration of lipids, N_A is Avogadro's number, and Δ_ρ is the scattering length difference, which can be calculated from the electron number and the molecular weight of the lipid and the solvent. The term υindicates the partial specific volume of the micelles in the solution, which can be determined by the density of the micellar solutions and the solvent

Analytical Ultracentrifugation (AUC). Sedimentation equilibria of micells in 50 mM NaCl were studied in a Beckman Optima XL-1 ultracentrifuge at 25 °C. A 12 mm double-sector cell was used, and the liquid column was adjusted to 2.0 mm. The rotor speeds were set at 2.0 × 10^4 rpm. The apparent weight-average molecular weight $M_{app,w^{-1}}$ and Q ($=M_{app,w}/M_{app,z}$) were determined by analyzing the Rayleigh fringe according to the established method.

Atomic Force Microscopy (AFM) Observations. A PPPNCHR 10 M cantilever (Park Systems) was used to observe the AFM images. Before AFM observation, the sample was spin-coated with 1500 rpm onto a freshly cleaved Muscovite Mica. The AFM images were recorded with a resolution of 1024 × 1024 pixels on the AFM operation in tapping mode in air at room temperature (RT) by using moderate scan rates (0.3 Hz).

Table S1 Fitting parameter of binary mixtures.

	α	R_g /nm	model	R_c/nm	R_s/nm	$R_s - R_c$ /nm	ρ_c/e nm^{-1}	ρ_s/e nm^{-1}
SC5	0	1.79	Sphere	0.85	2.3	1.45	272	363
QA7_5% in SC5	0	1.88	Sphere	0.9	2.5	1.6	270	365
QA7_10 % in SC5	0	2.04	Sphere	0.95	2.6	1.65	270	365

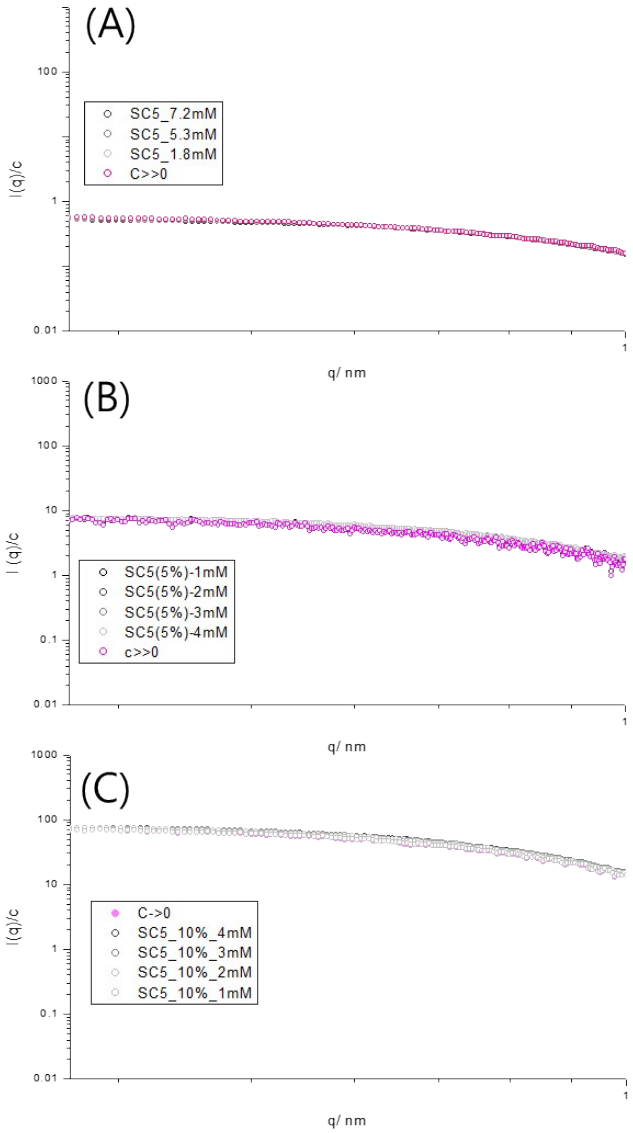

Fig. S1 $I(q)/c$ as a function of q for different concentrations in 50 mM aqueous NaCl ; (A) SC5, (B) 5% of QA7 in SC5 and (C) 10% of QA7 in SC5.

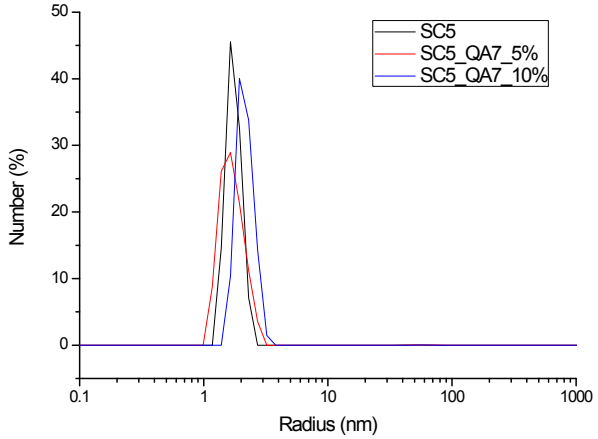

Fig. S2 DLS measurement of micelles; SC5, 5% of QA7 and 10% of QA7 in SC5.

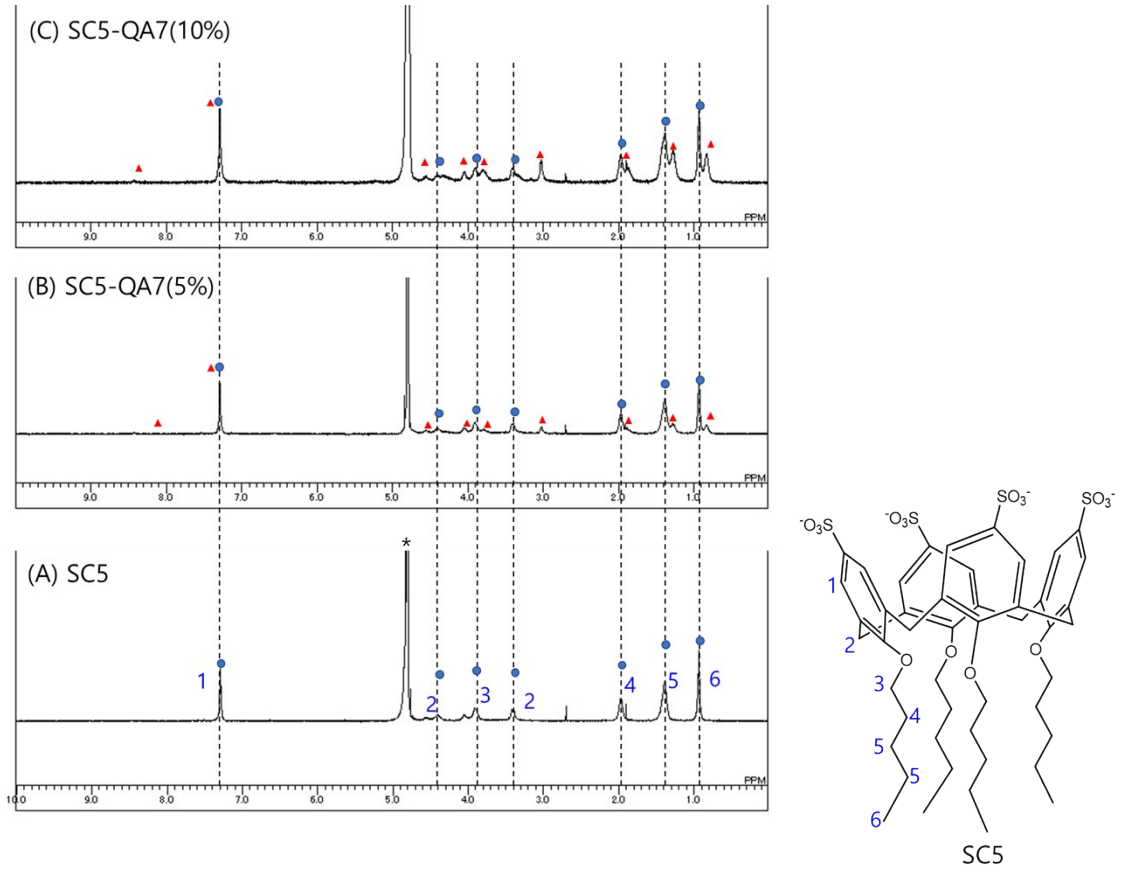

Fig S3. NMR measurement of (A) SC5, (B) SC5-QA7 (5%) and (C) SC5-QA7 (10%); blue symbol: peaks from SC5, red symbol: peaks from QA7.

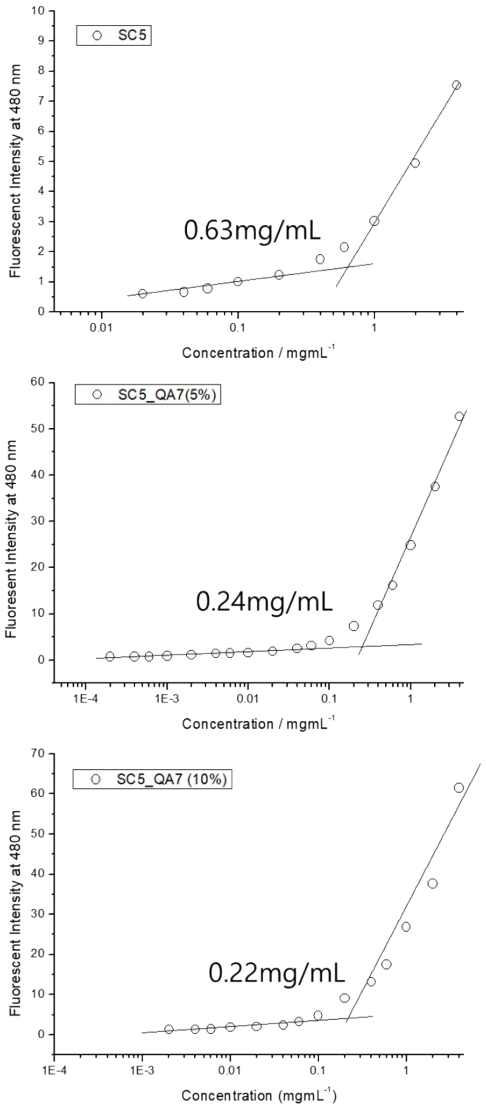

Fig. S4 CMC measurement of micelles; SC5, 5% of QA7 and 10% of QA7 in SC5.