Electronic Supplementary Material (ESI) for Soft Matter.

A Tetramer Micelle: The Smallest Aggregation Number Corresponding to the Vertex Number of Regular Polyhedra in Platonic Micelles

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General considerations

Materials and Synthesis. All chemical reagents were purchased from Tokyo Chemical Industry Co. and Sigma-Aldrich Co., which were used without further purification. The chemical reactions for the synthesis of sulfonatocalix[4]arene-based amphiphiles was carried out under nitrogen atmosphere. The progress of the reactions was monitored using thin layer chromatography (TLC), and detected using ultraviolet (UV; 254 nm) irradiation. Nuclear magnetic resonance spectra were recorded with a 500 MHz Bruker spectrometer using D_2O as solvents.

Synthesis of SC4AP (I).[1] A solution of sulfonatocalix[4]arene (0.300 g, 4.03×10^{-4} mol), 1-bromo pentane (1.33 g, 8.06×10^{-3} mol), sodium hydride (0.322 g, 8.06×10^{-3} mol), and anhydrous dimethyl sulfoxide (15 mL) was stirred at room temperature for 24 h under nitrogen atmosphere. The reaction solution was dried out by vacuum, and then the reactant powder was washed by ethanol., which afforded SC4AP as a white solid (0.390 g, 3.50×10^{-4} mol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (s, 1H), 5.36 (d, J = 7.88 Hz, 1H), 4.14 (s, 1H), 4.04 (m, 2H), 2.43–2.26 (m, 2H), 2.21 (t, J = 2.54 Hz, 1H), 2.11–1.85 (m, 2H), 1.44–1.43 (m, 18H). ESI–MS ($M^{2-}/2$): calcd for $C_{48}H_{60}Na_2O_{16}S_4^{2-}$ 533.13, found 533.3

Critical micelle concentration (CMC) measurements. The powder of SC4AP was dissolved in 10 mM aqueous NaCl to be 10 $mgmL^{-1}$ concentration, and the solution was diluted to be required concentration. 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. Before the fluorescence measurements, all samples were incubated for at least 30 min in the dark at room temperature. 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 SC4AP concentration.

Small angle X-ray scattering (SAXS) measurements. The powder of SC4AP was dissolved in 10 mgmL^{-1} aqueous NaCl to be required concentration. The prepared samples were left for at least one day to equilibrate at room temperature. Small angle X-ray scattering (SAXS) measurements were carried out at the BL-40B2 beamline of the SPring-8 facility, Hyōgo Prefecture, Japan. A 30 × 30 cm 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. The detailed experimental procedures are reported elsewhere.[2] The absolute SAXS intensities were recorded using the absolute scattering intensities of water.[3, 4]

The micellar SAXS profiles were fitted to core-shell spheres by using the following expression:

$$I(q) = \left\{ 3V_{\mathrm{C}}(\rho_{\mathrm{C}} - \rho_S)\frac{j_1(qR_{\mathrm{C}})}{qR_{\mathrm{C}}} + 3V_{\mathrm{S}}\rho_{\mathrm{S}}\frac{j_1(qR_{\mathrm{S}})}{qR_{\mathrm{S}}} \right\}^2 \quad (1)$$

Here, R_{c} and R_{s} are the outer radii of the core and micelle (core + shell), and ρ_{c}, ρ_{s}, and ρ_{sol} are the electron density of the core, the shell, and the solvent, respectively. j_1 are the second spherical Bessel function, respectively. V_{c} and V_{s} are the particle volume of the core and micelle (core + shell), respectively. For the core-shell sphere model, R_{g} is related to R_{c} and R_{s} by the following equation[5]:

$$R_g^{\,2} = \frac{3[V_{\mathrm{C}}R_{\mathrm{C}}^{\,2}(\rho_{\mathrm{C}} - \rho_{\mathrm{S}}) + V_{\mathrm{S}}R_{\mathrm{S}}^{\,2}\rho_{\mathrm{S}}]}{5[V_{\mathrm{C}}(\rho_{\mathrm{C}} - \rho_{\mathrm{S}}) + V_{\mathrm{S}}\rho_{\mathrm{S}}]} \quad (2)$$

The SAXS profiles in the low q region follow the Guinier relation given by the following equation:

$$I(q) = I(0)\exp(-q^2R_{\mathrm{g}}^{\,2}/3) \quad (3)$$

where $I(0)$ is the forward scattering intensity at $q = 0$. $I(0)$ and the gyration radius (R_g) are determined from the intercept and the slope of the $\ln(I(q))$ vs. q^2 plot (Guinier plot). Due to inter-particle interference, the $I(0)$ and R_g values depend on the sample concentration. In order to remove the concentration effects, the SAXS intensities recorded at different concentrations were extrapolated to zero concentration.

Determination of micellar molar mass by SAXS. The molar mass of the micelles can be given by the following equation:

$$M_w = I(0)\{N_A c(\Delta\rho\bar{\upsilon})^2\} \quad (4)$$

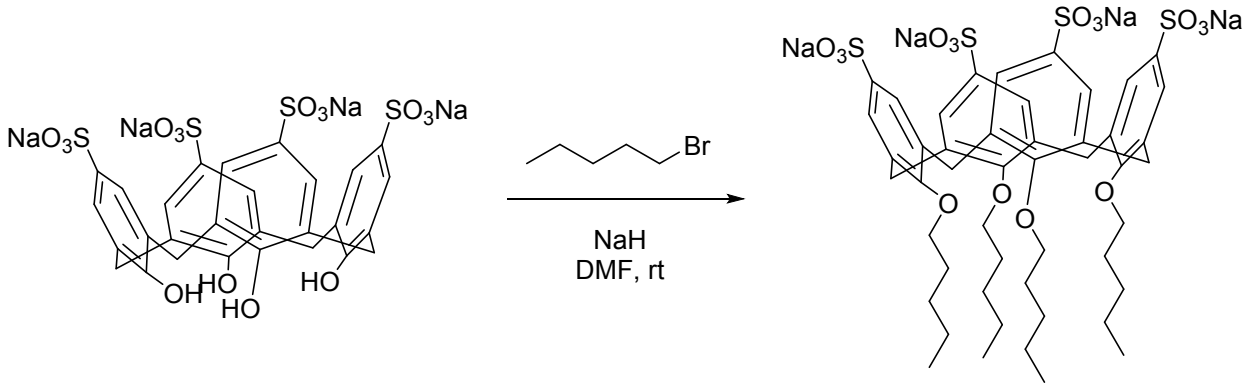
Where M_w is weight averaged molecular weight, c is the concentration of lipids, N_A is Avogadro's number, and $\Delta\rho$ is the scattering length difference, which can be calculated from the electron number and the molecular weight of the lipid and the solvent. The term $\bar{\upsilon}$ indicates the specific volume of micelles in the solution, which can be determined by the density of the micellar solutions and the solvent (Figure S3).

Multi-angle light scattering coupled with asymmetric flow field flow fractionation (AF4-MALS) measurements. SC4AP (10 mg mL^{-1}) was prepared in 10 or 15 mM aqueous NaCl. Aliquots (30 μL) of the sample solution were immediately injected into an Eclipse 3+ separation system (Wyatt Technology Europe GmbH, Dernbach, Germany) for field-flow fractionation (FFF) at 25°C. The output from FFF was then passed sequentially through a Dawn Heleos II multiangle light-scattering (MALS) detector (Wyatt Technology), UV detector, and an Optilab rEX DSP differential refractive index (RI) detector (Wyatt Technology), operating at a wavelength of 658 nm. A Wyatt channel (Eclipse 3 channel LC) attached to a membrane (polyether sulfone membrane; 1 kDa LC) at the bottom of the channel was used for the measurements. The cross-flow and channel-flow rates were fixed at 4.0 and 1.0 mL min^{-1}, respectively. Detailed experimental procedures are reported elsewhere.[6] The

specific refractive index increments ($\partial n/\partial c$) and the extinction coefficients (ε at 270 nm) of the micelles in aqueous solution were determined using a DRM-1021 differential refractometer (Otsuka Electronics, Osaka) and a Jasco V-630 spectrometer, respectively (see Figure S3).

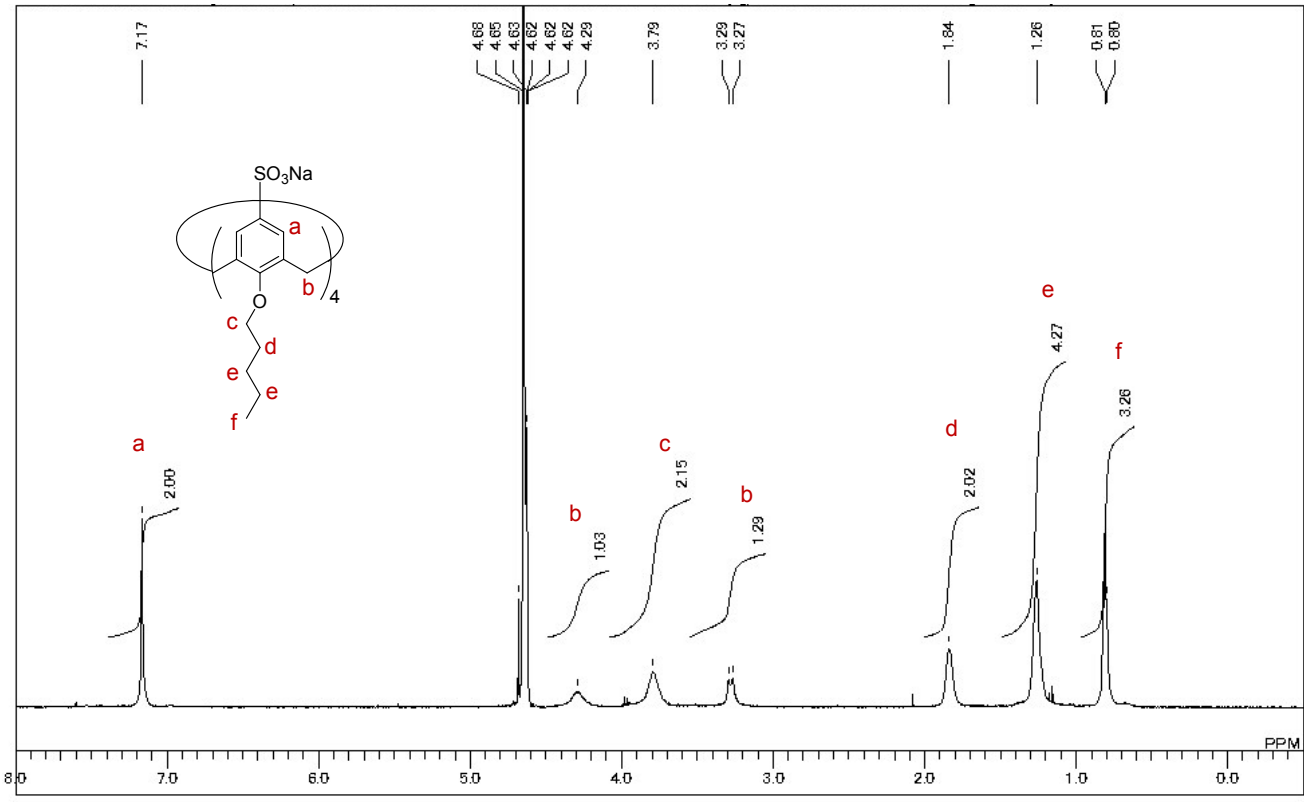
Analytical ultracentrifugation (AUC). Sedimentation equilibriums of SC4AP in 10 or 15 mM NaCl was studied in a Beckman Optima XL-1 ultracentrifuge at 25 °C. A 12 mm doublesector cell was used and the liquid column was adjusted to 2.0 mm. The rotor speeds were set at 2.0×10^4 rpm. From analyzing the Rayleigh fringe, the apparent weight average molecular weight $M_{w,App}$ and Q (= $M_{w,App}/M_{z,App}$) were determined according to the established method.[7]

Synthesis Scheme



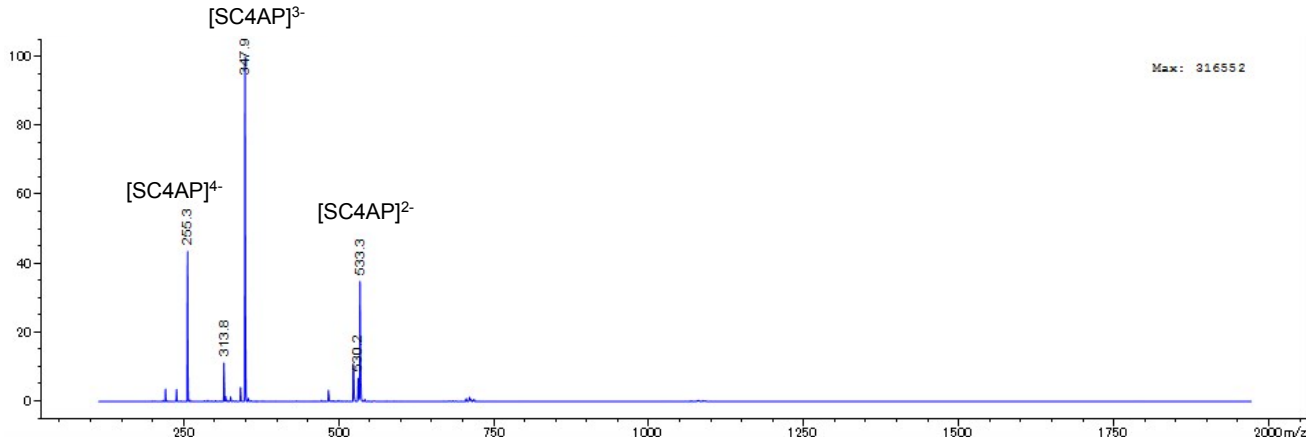
Schem S1. Synthesis schem of sulfonatocalix[4]arene based amphiphiles (SC4AP).

NMR spectrum



[1]H-NMR spectrum of compound SC4AP.

MS spectrum



Mass spectrum of SC4AP

Figure S1

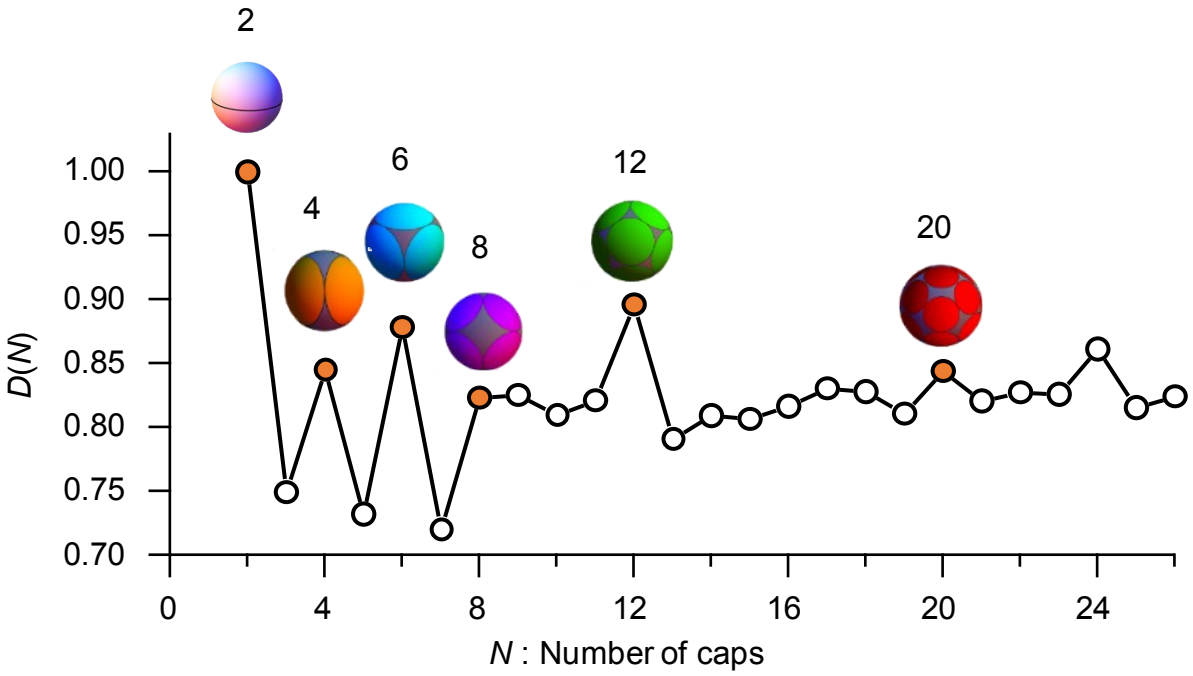


Figure S1. *D*(*N*) for *N* ranging from 2 to 26. Certain numbers produce a local maximum and are identical to the number of the vertices of Platonic solids.

Figure S2

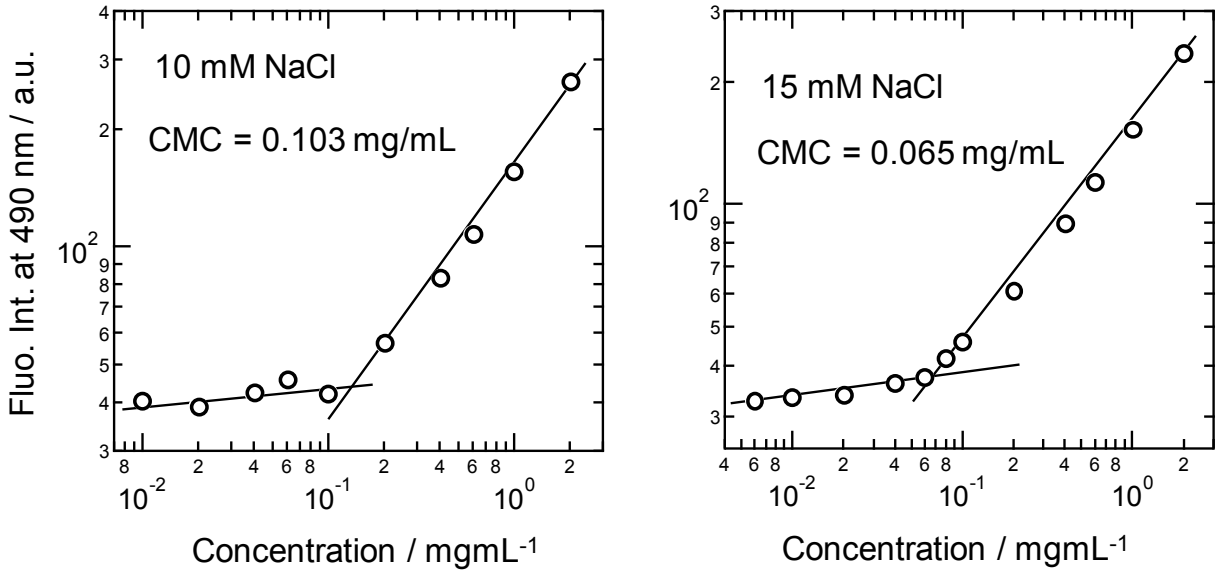


Figure S2. The fluorescence intensity of the ANS spectra at 470 nm plotted against the concentration of SC4AP in 10 (left) and 15 (right) mM aqueous NaCl.

Figure S3

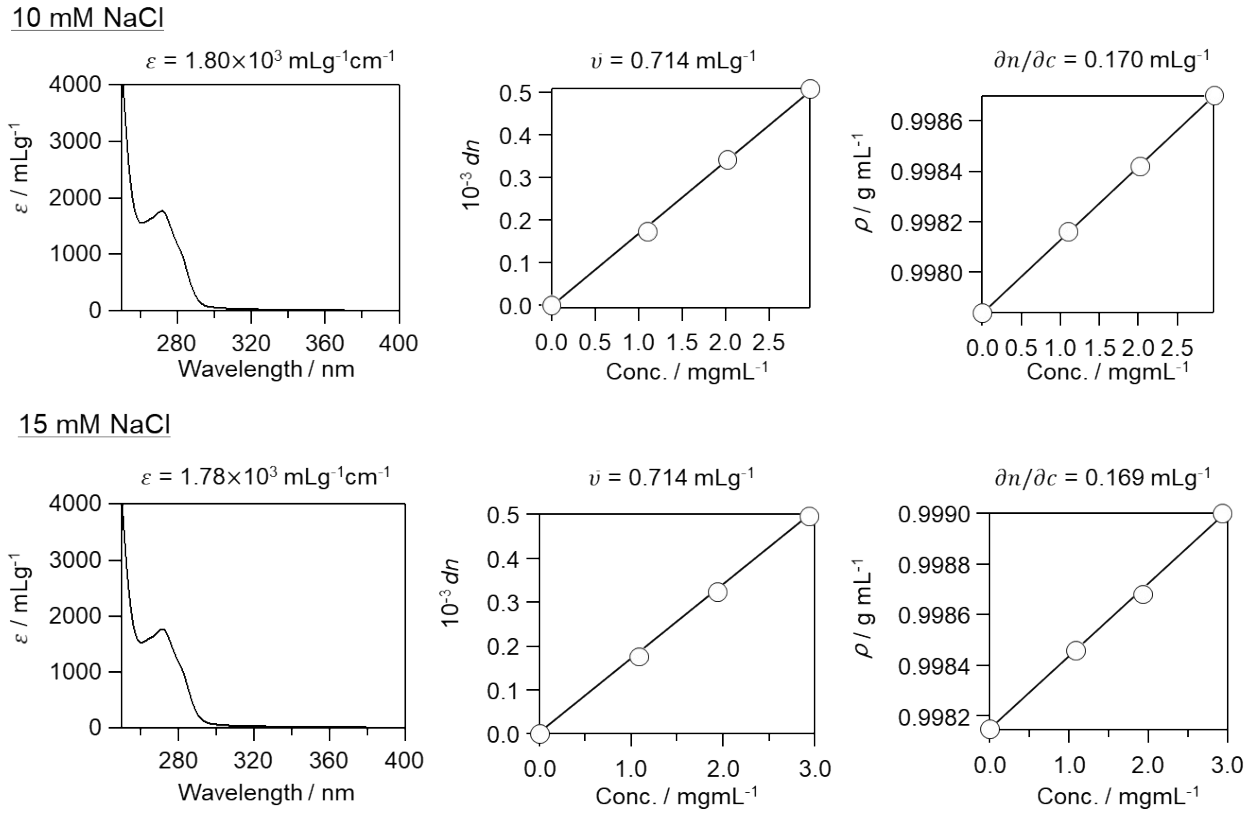


Figure S3. UV-vis profiles and concentraton dependence of refractive index increment and density increment for SC4AP in 10 and 15 mM aqueous NaCl.

Figure S4

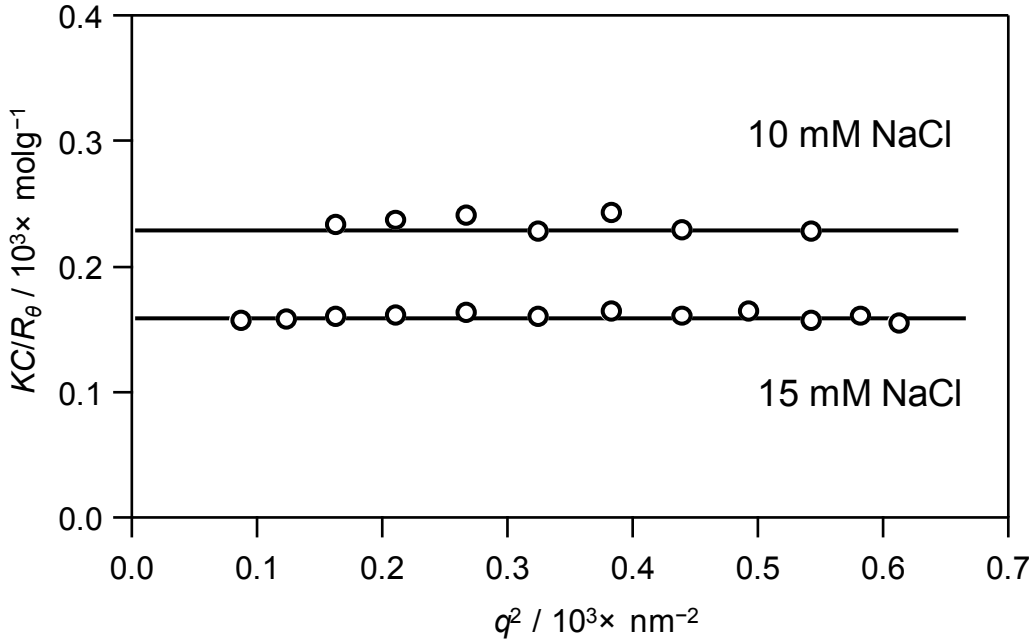


Figure S4. The Zimm plots for SC4AP micelles in 10 or 15 mM aqueous NaCl at the top of the LS peaks.

Figure S5

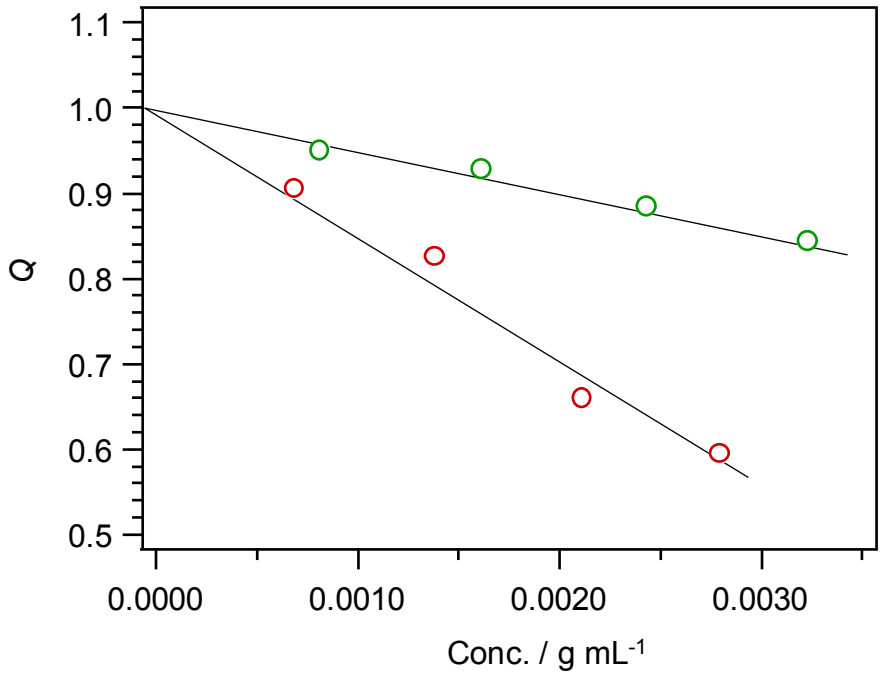


Figure S5. The concentration dependence of Q (= $M_{w,App}/M_{z,App}$) determined by analytical ultracentrifugation measurements for SC4AP micelles in 10 (red) or 15 (green) mM aqueous NaCl solutions.

Figure S6

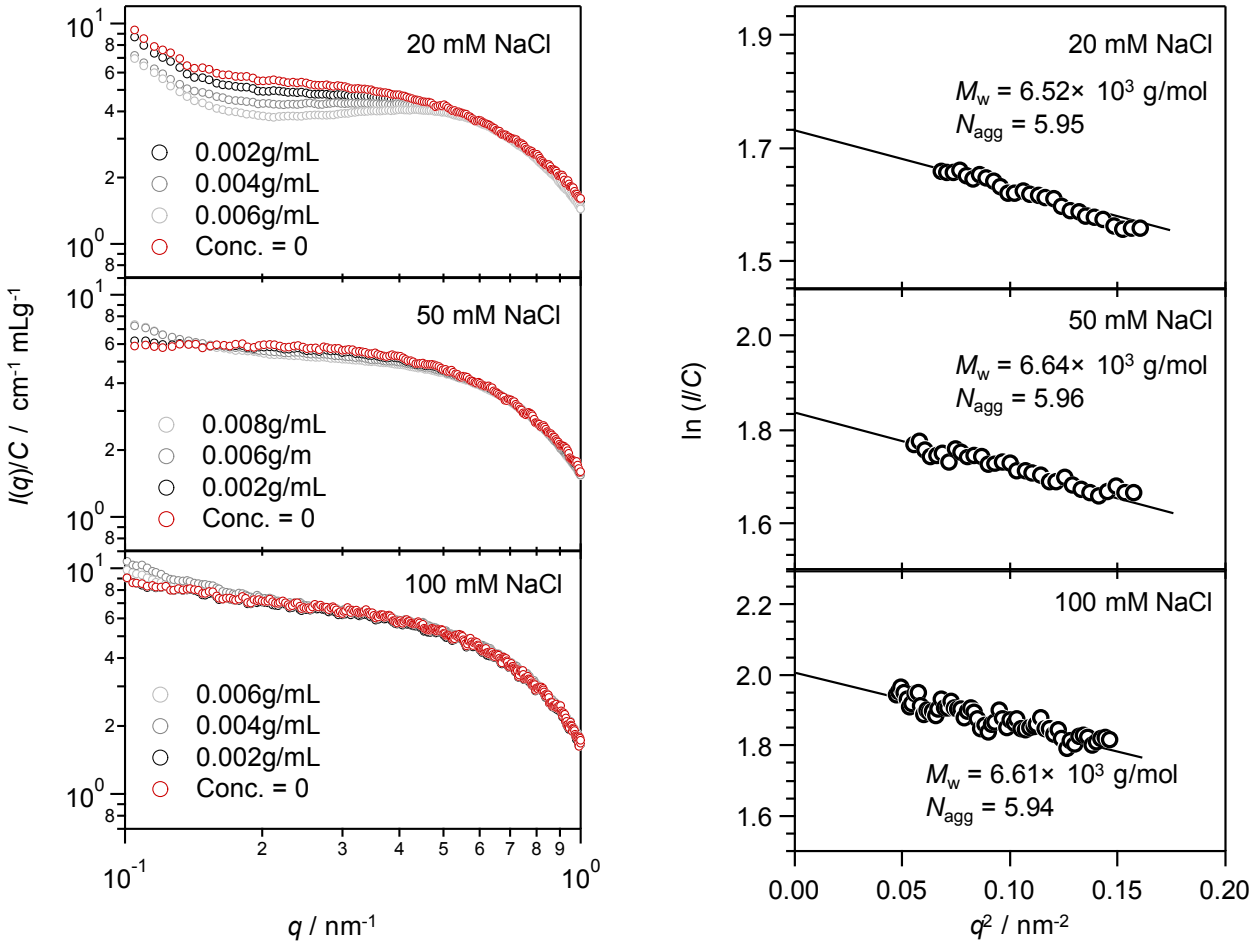


Figure S6. Left side: $I(q)/c$ as a function of q for different SC4AP concentrations in 20, 50, and 100 mM NaCl solution. The extrapolated values at infinite dilution for each q are shown by the red markers. Right side: Guinier plot (i.e., ln $I(q)/c$ versus q^2) constructed from the extrapolated intensities. The micellar molar mass determined from the intercept values at $q = 0$.

References

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7. H. Fujita.