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Tuning of the aggregation number of Platonic micelles with binary mixture of calix[4]arene surfactants

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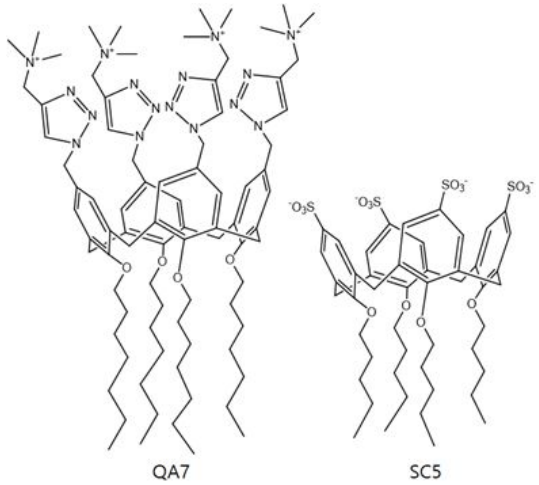
The mixture ratios were used as a factor for aggregation number (N_{agg}) determination in binary mixtures of calix[4]arene surfactants. Platonic micelles having different N_{agg}were prepared by adjusting the ratio of oppositely charged compounds.

Colloid science is the study of systems involving small particles. When the colloids are aggregated, depending on the structure of the surfactant molecules, micelles of different shapes, such as spherical, cylindrical, hexagonal, and cubic lamellar, can be formed[1, 2, 3, 4, 5, 6]. The size of a micelle is related to the aggregation number (N_{agg}) or the molecular weight of the micelle. Among the different types of micelles, our group recently focused on spherical micelles using calix[4]arene molecules with N_{agg} values being selected from among 4, 6, 8, 12, 20, and 32[7, 8, 9]. Interestingly, some of these numbers match the face numbers of Platonic solids, so we named them "Platonic micelles."

Several studies on the control of N_{agg} using Platonic micelles have been reported. To change N_{agg}, we attempted to change various factors, such as (1) the salt concentration of solvent[10, 11], (2) headgroup repulsive force[12], (3) hydrophobic tail length[7], (4) pH[13], and (5) temperature[8].

Takahashi et al. reported the salt-induced increase in N_{agg} of micelles formed from calixarene-derived surfactants by a stopped-flow device coupled with time resolved small angle x-ray scattering[11]. The results revealed that a transition from a dodecamer ($N_{agg} = 12$) to an icosamer ($N_{agg} = 20$) was induced by a rapid increase in the NaCl concentration. Yoshida et al. employed polyethylene glycols (PEGs) as the nonionic headgroup of calix[4]arene-based amphiphiles to study the effects of only repulsive interactions caused by steric hindrance on the formation of Platonic micelles[12]. The amphiphiles containing relatively low-molecular-weight PEGs (550 or 1000 g mol^{-1}) formed dodecamer ($N_{agg} = 12$) or octamer ($N_{agg} = 8$) micelles, respectively, with no variation in the N_{agg}. Fujii et al. reported the pH-controllable N_{agg} of micelles showing hexamer ($N_{agg} = 6$) and dodecamer ($N_{agg} = 12$) micelles[13]. Thus far, we have controlled various variables for aggregate control in a system of single kind of surfactant, such as anionic surfactant, cationic surfactant, and nonionic surfactant. However, in this study we attempt to resolve whether we can produce Platonic micelles in a mixed system.

In this paper, we describe a study of N_{agg} of binary mixtures of calix[4]arene surfactants having opposite electric charges. The surfactants with opposite electric charges were mixed with each other, so we expected that the N_{agg} may change relative to that for a single molecule when spherical micelles were produced. We used two calixarene-derived molecules having sulfonic groups (SC5) and quaternary amine groups (QA7). The N_{agg} of sulfonic calix[4]arene having five alkyl chains is 6 under the condition of 50 mM NaCl solvent. We mixed a quaternary amine calix[4]arene, which has



QA7 SC5

seven alkyl chains, with sulfonic calix[4]arene, which was in an enriched state. In previous work, we observed the morphological

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transitions when comparable amounts of cation surfactant and anion surfactant were mixed[14]. For this reason, we arranged the proportion of QA7 in the mixture to be within 10% in SC5. When the total amount of QA7 was within 10%, the spherical shape of the micelles was maintained. If the proportion of QA7 were to surpass 10%, this may lead the packing parameter to exceed 1/3, which would result in a morphological transition. Therefore, we prepared 5% and 10% QA7 in SC5.

We observed the morphologies of spherical micelles in different mixtures, namely, 5% and 10% QA7 in SC5, by atomic force microscopy (AFM). As shown in Fig. 1, spherical micelles were observed. The micelles all had a size of approximately 3–4 nm and also had a uniform shape.

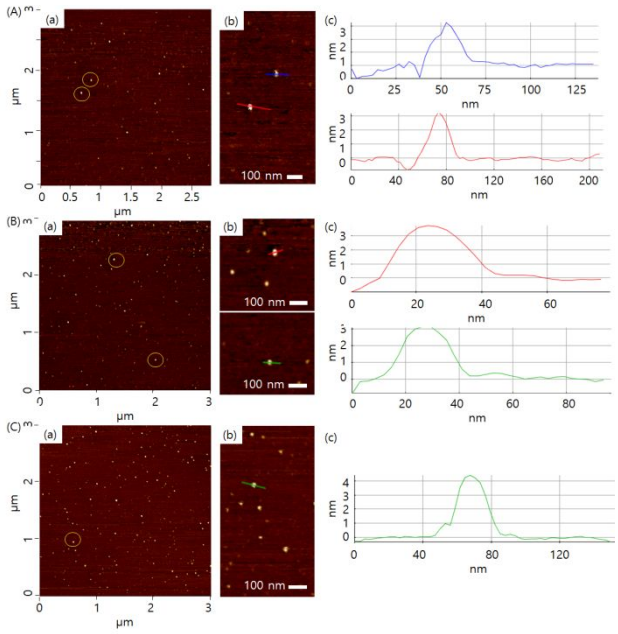

Fig. 1 AFM images of (A) SC5, (B) SC5_QA7 (5%), and (C) SC5_QA7 (10%); (a, b) original images and (c) thickness of micelles.

Fig. 2A shows the SAXS profiles of the micelles in 50 mM NaCl solution with an increasing proportion of QA7. The slope (α) was zero from the SAXS intensity in the low-q region, where the scattering intensity, $I(q)$, is expressed as $I(q) \propto qa$. This indicates that these solutions contain isolated scattering objects without secondary aggregation; these objects are probably spherical micelles. The SAXS profiles were fitted to the core–shell spherical model.

$$I(q) \propto \left[V_c(\rho_c - \rho_s)\frac{3j_1(qR_c)}{qR_c} + V_s(\rho_s - \rho_0)\frac{3j_1(qR_s)}{qR_s}\right]^2$$

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 densities of the core, the shell, and the solvent, respectively. j_1 is the second spherical Bessel function. V_c and V_s are the particle volumes of the core and micelle (core + shell).

The scattering profiles of micelles extrapolated to zero concentration are shown in Fig. S1, and the weight-averaged molar masses (M_w) of the micelles in 50 mM NaCl are determined from the intercept values [I(0)] obtained by extrapolating the scattering intensity to zero angle

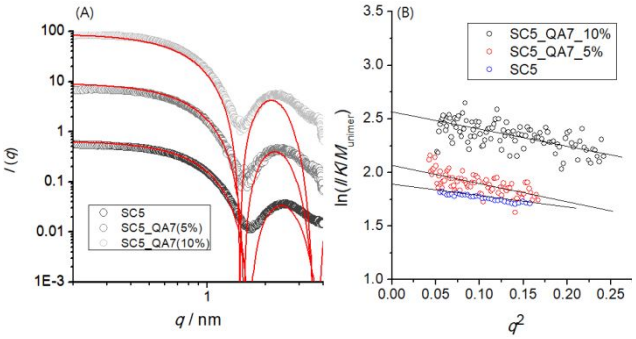

Fig. 2 (A) SAXS profiles for SC5 with increasing QA7 (0%, 5%, and 10%) in 50 mM NaCl. The solid lines were plotted using the core–shell sphere model. (B) Guinier plot (i.e., ln$I(q)/c$ versus q^2) constructed from the extrapolated intensities.

to be 6,900 g mol^{-1} at SC5, 10,045.7 g mol^{-1} at 5% QA7 in SC5, and 15,996.2 g mol^{-1} at 10% QA7 in SC5 (Fig. S1). These results led us to conclude that the aggregation numbers of the micelles are 6.0, 8.0, and 12 at SC5, 5% QA7 in SC5, and 10% QA7 in SC5, respectively. Even in a mixed system of calix[4]arene-based lipids, Platonic micelles can form and show monodispersity in terms of the aggregation numbers, which are consistent with the vertex numbers of Platonic solids (6, 8, and 12). Fig. 2B presents a comparison of the Guinier plot for the different compositions with an increasing proportion of QA7 in SC5. For the core–shell sphere model, R_g is related to R_C and R_S by the following equation:

$$R_g^2 = \frac{3[V_s Rc^2(\rho_c - \rho_s) + V_s R_s^2 \rho_s]}{5[V_c(\rho_c - \rho_s) + V_s \rho_s]}$$

The values of R_C and R_S obtained by fitting (Table S1) the calculated values of Rg were 1.79, 1.88, and 2.04 nm upon increasing the proportion of QA7 from 0% to 10%. The q value associated with the first minimum (q first min) is related to the micelle size. The q first min was shifted from 1.51 to 1.68 nm^{-1}. This is consistent with the size change observed in the Guinier region. R_h values of the micelles were also measured by dynamic light scattering (DLS) (Fig. S2), which were 1.8, 2.0, and 2.3 nm, respectively.

Table 1. Molar Masses Determined with Different Methods and Aggregation Numbers

	SAXS	AUC		N_{agg}
	M_w	M_w	M_z/M_w	
SC5	6,900.6	6,924	1.04	6
QA7_5% in SC5	10,045.7	10,067	1.03	8
QA7_10% in SC5	15,996.2	15,758.28	1.05	12

We also performed analytical ultracentrifugation (AUC) measurements for different compositions of calix[4]arene lipids. Fig. 3A presents the concentration dependence of the apparent weight-averaged molecular weight (M_w, App), where M_z, App is the apparent z-averaged molecular weight (M_z). The values of the molar mass were 6,924 g mol^{-1} for SC5, 10,067 g mol^{-1} for 5% QA7 in SC5, and 15,758 g mol^{-1} for 10% QA7 in SC5, being consistent with those determined by SAXS measurements. As shown in Table 1, the calculated molecular weight distribution (M_z/M_w) was almost 1.0 for all micelles. The agreement of the molar mass values in the two independent measurements led us to conclude that the N_{agg} of micelles with an increasing proportion of QA7 in SC5 were 6, 8, and 12, respectively (Fig. 3B).

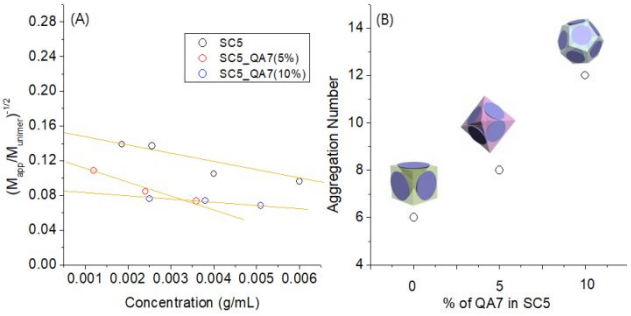

Fig. 3 (A) The concentration dependence of M_w, App determined by AUC measurements for micelles in 50 mM NaCl. (B) Plot of N_{agg} with increasing rate of QA7 in SC5.

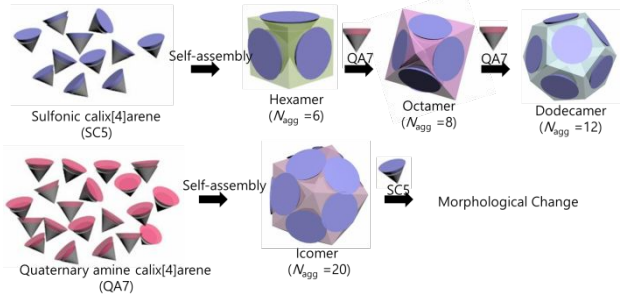

Fig. 4 The change in N_{agg} in binary mixtures of Platonic micelles.

NMR was measured in the expectation that the intermolecular interaction would cause some chemical shift when small amounts of cationic surfactants were added in an excess of anionic surfactants. Unfortunately, we couldn't observe any chemical shift in NMR (Fig. S3).

The critical micelle concentration (CMC) of the different compositions of micelles was determined with 8-anilinonaphthalene-1-sulfonate as a fluorescence probe (Fig. S4). The CMC values were 0.63, 0.24, and 0.22 mg/mL for SC5, 5% QA7 in SC5, and 10% QA7 in SC5, respectively. In the mixed system, the CMC was lower than that obtained for the free system (only SC5) because the small amount of oppositely charged surfactant induced only a small change of the intermolecular electrostatic repulsions due to the opposite charge of surfactants. As mentioned above, over 10% QA7 in SC5 led to morphological transition. In addition, in a system with the opposite characteristics, namely, an abundance of QA7 added to SC5, morphological transition can occur, despite the presence of a small amount of SC5. This is because of the repulsive headgroup of QA7. In this case, when QA7 formed spherical micelles, its N_{agg} was 20.

In conclusion, we prepared binary mixtures of calix[4]arene surfactants having opposite electric charges. When the surfactants with opposite electric charges were mixed with each other, we demonstrated that the N_{agg} changed from 6 to 8 and 12. The preferred N_{agg} values were explained in relation to the mathematical Tammes problem[15]. This can be obtained the best coverage of a sphere surface with multiple identical circles. The coverage ratio $D(N)$ can be calculated maxima at N = 6, 8 and 12, matching with the observed N_{agg} values. These results are in accordance with the principle of Platonic micelles, meaning that the opposite electric charges are also an example of the change of N_{agg}. However, when the N_{agg} was 20, despite addition of the oppositely charged surfactant, there was no change of N_{agg}. This resulted in the morphological transition.

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Graphical abstract