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Structural Study on Aggregation Behavior of Star-Type Trimeric Surfactant in the Presence of Sodium Salicylate

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Abstract

We investigated the aggregation behavior of star-type trimeric surfactants (3C_{12}trisQ) with a hydrocarbon chain length \((n)\) of 12 in sodium salicylate (NaSal) aqueous solution at various surfactant \((C_D)\) and salt concentrations \((C_S)\) using small-angle X-ray scattering (SAXS) and rheological measurements. At a low surfactant concentration \((C_D = 7 \text{ mM})\), 3C_{12}trisQ aggregates in solution evolved from ellipsoidal micelles, to rodlike or wormlike micelles and finally to multi-lamellar vesicles (MLVs) with increasing \(C_S\). In contrast, at higher surfactant concentrations \((C_D = 14 \text{ and } 28 \text{ mM})\), we did not observe vesicle formations of 3C_{12}trisQ because 3C_{12}trisQ were insoluble in solution at higher NaSal concentrations. The structural transitions of the 3C_{12}trisQ aggregates strongly depended on both \(C_S\) and \(C_D\). We also compared the MLV structure formed by 3C_{12}trisQ with that formed by gemini-type surfactants (12-2-12). The repeat distance of the 3C_{12}trisQ MLV (33.95 Å) was remarkably larger than that of the 12-2-12 (22.36 Å). We found that introducing spacer chains, i.e., from dimeric to trimeric surfactants, caused a decrease in NaSal concentrations at which micelle-to-vesicle transitions were observed.
1. Introduction

Surfactants are known to form various types of aggregated structures in aqueous solutions, such as spherical micelles, wormlike micelles, and vesicles. In particular, wormlike micelles formed by cationic surfactants in solutions with a small amount of particular salts, such as sodium salicylate (NaSal), have been extensively studied by rheological measurements, cryogenic transmission electron microscopy (cryo-TEM), freeze fracture TEM (FF-TEM), small-angle neutron scattering (SANS), nuclear magnetic resonance (NMR), and calorimetry [1–7]. Rheological measurements have shown that wormlike micelles behave similar to linear polymers. However, a marked difference in rheology is that wormlike micelles undergo phantom crossing, branching, and micellar growth. Given their rheological properties, wormlike micelles have been applied as drag reducing agents [8–10] and as templates for mesoporous silica [11,12].

Similar to their monomeric counterparts, gemini-type surfactants have attracted considerable attention because of their unique physicochemical and rheological properties. Gemini-type surfactants consist of two hydrophilic head groups and two hydrophobic chains connected by spacer chains. Under salt-free conditions, cationic gemini-type surfactants with a hydrocarbon chain length \(n\) of 12 \(12-2-12\) form spherical and wormlike micelles at lower and higher surfactant concentrations, respectively. Several studies have compared the formation mechanisms of wormlike micelles of monomeric surfactants with \(n = 12\) in organic salt solutions with those of \(12-2-12\) in salt-free solutions [13–15]. MacKintosh et al. reported that additional salts
influence wormlike micellar growth by altering both the surface charges and the end-cap energies of wormlike micelles [16]. Since the end-cap energy can be manipulated by the number of spacer chains, we synthesized star-type trimeric surfactants (3CₙtrisQ) consisting of three hydrocarbon chains and three hydrophilic groups connected by spacer chains [17]. We also investigated the growth mechanisms of wormlike micelles formed by 3C₁₂trisQ in salt-free aqueous solutions by SANS and rheological measurements. We observed a sphere-to-rod transition of 3C₁₂trisQ micelles as a result of water extrusion from the micelle. Furthermore, we found that the end-cap energy is higher in wormlike micelles formed by the trimeric surfactant compared with those formed by the gemini-type surfactant with the same number of hydrocarbon chains [14].

The salt effect on the structures of gemini-type surfactant aggregates has also been investigated [7,18–20]. Yu et al. studied the effects of four salts on the aggregation behavior of two gemini surfactants (12-4-12 and 12-4(OH)₂-12) [20]. They reported that a micelle-to-vesicle transition was triggered by the penetration of salt (i.e., NaSal) anions into the surfactant and the subsequent charge neutralization. Lu et al. reported that 12-2-12(Et) could also form various structures in solution containing NaSal [7]. To clarify the effect of NaSal on the formation mechanisms (including micelle-to-vesicle transitions) of cationic surfactant aggregates in solution, the structural behaviors must be compared among monomeric, gemini, and trimeric surfactants. However, investigations on trimeric surfactants have been largely neglected to date.
In the present study, we investigated the aggregation behavior of 3C_{12}trisQ in solutions containing NaSal by rheological measurements at different surfactant (C_D) and salt concentrations (C_S). In addition, using small-angle X-ray scattering (SAXS) technique, we investigated the structural evolution during NaSal-induced a sphere-to-rod transitions of 3C_{12}trisQ micelles at low sample concentrations. We then compared the structures of multi-lamellar vesicles (MLVs) formed by 3C_{12}trisQ with those formed by 12-2-12.

2. Material and methods

2.1. Chemicals and materials

A trimeric surfactant, 3C_{12}trisQ, with a hydrocarbon chain length of 12 and a spacer chain length of 2, was synthesized as previously reported [17]. The chemical structure of 3C_{12}trisQ is presented in Figure 1. The details of the synthetic procedure,

![Figure 1](image_url)

**Figure 1.** Chemical structure of a star-type trimeric surfactant, tris(N-dodecyl-N,N, N-dimethyl-2-ammoniumethyl)amine bromide (3C_{12}trisQ). The spacer chain length is set to 2.
interfacial properties, and aggregation structure of 3C₆trisQ in aqueous solution are described in our previous study [17]. The NaSal was purchased from Wako Pure Chem. Industries, Japan.

2.2. Rheology measurements

Rheological experiments were performed using a stress-control rheometer (MCR-501, Anton Paar, Austria) equipped with a cone plate with a radius of 25.0 mm and a cone angle of 1°. The shear rate was varied from 0.01 to 1000 s⁻¹. The sample temperature was controlled at 25.00 ± 0.03°C.

2.3. SAXS measurements

SAXS measurements were conducted using the SAXS instrument installed on the BL40B2 beamline at SPring-8, Sayo, Hyogo, Japan [21]. The X-ray wavelength was 0.7 Å, and the sample-to-detector distance (SDD) was 2.1 m. The covered $q$ range was $q = 0.008–0.6$ Å⁻¹ (where $q = (4\pi/\lambda)\sin(\theta/2)$, in which $\lambda$ and $\theta$ represent the wavelength and scattering angle, respectively). The accessible lower $q$ limit ($q_{\text{min}}$) depended on the instrumental background. The exposure time for each sample was 3 min. We also performed SAXS measurements using the SAXS instrument installed on the BL10C beamline at Photon Factory (PF), Tsukuba, Ibaraki, Japan [22]. An X-ray beam with $\lambda$ of 1.49 Å was used, and the SDD was 1.0 m. The covered $q$ range was $q = 0.013–0.4$ Å⁻¹. The exposure time for each sample at PF was 7 min. In both SAXS experiments, the X-rays scattered from the samples were collected by an imaging plate detector
(R-AXIS VII, Rigaku, Tokyo, Japan). After circular averaging using *Fit2d* software [23], the solvent intensity was subtracted by taking account of the transmission. All measurements were performed at room temperature.

### 2.4. Model-fitting analysis of SAXS results

In general, the scattering intensity from an assembly of particles is given by

\[ I(q) = N_p P(q) S(q) \]  

where \( N_p \), \( P(q) \), and \( S(q) \) are the number density of particles, the form factor, and the structure factor, respectively. As shown in our previous reports, the 3C\(_{12}\)trisQ aggregates in salt-free aqueous solution were ellipsoidal or rodlike micelles in solutions [14,17]. We utilized the form factor \( P(q) \) of a core-shell particle model since the scattering length density of the shell portion remarkably differs from that of the core portion inner micelles. The form factor \( P_{el}(q) \) of a core-shell ellipsoid with core radius \( R_c \), axial ratio of core \( u_c \), and shell thickness \( T_s \) is given by

\[ P_{el}(q) = \frac{9}{q^2} \int_0^r \frac{\Delta \rho_s V_{tot}}{q r_{tot}} \left( \frac{\Delta \rho_s - \Delta \rho_c}{q r_c} \right) V_c \left[ j_1 \left( \frac{q r_{tot}}{q r_c} \right) - j_1 \left( \frac{q r_c}{q r_{tot}} \right) \right] dx \]  

where \( j_1(x) \) is the first-order spherical Bessel function of \( x \), \( \Delta \rho_s \) and \( \Delta \rho_c \) are the scattering contrasts of the shell and core portions, respectively, \( V_{tot} \) and \( V_c \) are the total volume of the micelle and the volume of the core portion, and \( r_{tot} \) and \( r_c \) are defined as

\[ r_{tot} = \left[ \left( R_c + T_s \right)^2 x^2 + \left( u_c R_c + T_s \right)^2 \left( 1 - x^2 \right) \right]^{1/2} \]  

and
When $3C_{12}\text{trisQ}$ molecules form spherical micelles in solution, the value of $u_c$ is 1. On the other hand, the form factor $P_{\text{rod}}(q)$ of a core-shell cylinder with radius of the cross-section of core $R_c$, the full length of the core $L_c$, and shell thickness $T_s$ is given by

$$P_{\text{rod}}(q) = \frac{\pi^2}{\phi} \int_0^{\frac{\pi}{2}} \left[ \Delta \rho \rho c \pi a q v c \left( \sin x \right) - (\Delta \rho - \Delta \rho c) v c \left( \sin x \right) \right]^3 \sin x dx$$

where

$$A_{\text{tot}}(q) = \frac{2J_1(q(R_c + T_s) \sin x)}{q(R_c + T_s) \sin x} \left[ \sin(q(L_c + T_s) \cos x / 2) \right]$$

and

$$A_c(q) = \frac{2J_1(qR_c \sin x)}{qR_c \sin x} \left[ \sin(qL_c \cos x / 2) \right]$$

Here, $J_1(x)$ is the first kind of cylindrical Bessel function of order 1.

The structure factor $S_{\text{HP}}(q)$ for a charged micellar system interacting through a repulsive screened Coulomb potential is given with the rescaled mean spherical approximation as follows [24,25]:

$$S_{\text{HP}}(q) = \frac{1}{1 - 24\phi a(q\sigma)}$$

where $\phi$ is volume fraction, $\sigma$ is the effective particle diameter, and $a(q\sigma)$ was given by Hayter and Penfold [24]. $a(q\sigma)$ depends on the volume fraction and the degree of ionization and gives the value of Debye length ($l_d$). The $l_d$ is given by

$$l_d = \left( \frac{\varepsilon \varepsilon_0 k_B T}{2N_A e^2 I} \right)^{1/2}$$

where $\varepsilon$ is the dielectric constant of the solvent, $\varepsilon_0$ is the permittivity of free space, $k_B$ is the Boltzmann constant, $T$ is the temperature, $N_A$ is the Avogadro constant, $e$ is the
electronic charge, and \( I \) is the ionic strength of the solution. For asymmetric particles, such as ellipsoidal or rod-shaped particles, the structure factor \( S'(q) \) is modified for anisotropic shapes. Therefore, \( S'(q) \) is given by \[26\]

\[
S'(q) = 1 + \frac{\left\langle F(q) \right\rangle^2}{\left\langle |F(q)|^2 \right\rangle} (S(q) - 1)
\]  

(10)

where \( F(q) \) is the scattering amplitude of the particle.

3. Results and Discussion

3.1. Aggregation behavior of 3C\textsubscript{12}trisQ in solution as a function of sample and NaSal concentrations: Rheological measurements

To reveal the dependences of the 3C\textsubscript{12}trisQ aggregates on the sample and salt concentrations, rheological measurements were conducted at various \( C_D \) and \( C_S \) values. Note that the shapes of 3C\textsubscript{12}trisQ aggregates in solution are sensitive to the share rate \( (\dot{\gamma}) \) [14]. Figures 2a–c show the viscosity changes in 3C\textsubscript{12}trisQ at \( C_D \) values of (a) 7 mM, (b) 14 mM, and (c) 28 mM as a function of the shear rate with various ratios of salt concentration to the surfactant concentration \((C_S/C_D)\). Here, the \( C_S/C_D \) ratio was increased from 0 to the NaSal solubility-limit concentration; beyond this concentration, NaSal is insoluble in water. The viscosity for water is also shown as a reference. At \( C_S/C_D = 0 \) (i.e., a case of salt-free solution), we determined the sample concentration \( (C_D) \) dependence of the aggregates based on the SANS profile of 3C\textsubscript{12}trisQ and found that 3C\textsubscript{12}trisQ formed ellipsoidal micelles at \( C_D = 7 \) mM, and rodlike (wormlike)
micelles at $C_D = 14$ and 28 mM [14].

Figure 2. Dependence of viscosity on shear rate for star-type trimeric surfactants (3C$_{12}$trisQ) in solutions containing NaSal with varying ratios ($C_S/C_D$) of salt ($C_S$) to surfactant ($C_D$) molar concentrations: (a) $C_D = 7$ mM, (b) $C_D = 14$ mM, and (c) $C_D = 28$ mM. Results for pure water are shown as a solid line.

As shown in Figure 2a, in the region of $C_S/C_D \leq 0.24$, the viscosity of the 3C$_{12}$trisQ solution at $C_D = 7$ mM was independent of the shear rate and very close to that of water, implying that the 3C$_{12}$trisQ aggregates were spherical (ellipsoidal) micelles. At $C_S/C_D =$
0.3, the viscosity obviously exceeded that of water, but remained independent of the shear rate; hence we considered these aggregates to be rodlike micelles. Cationic surfactants are known to undergo sphere-to-rod transitions in the presence of NaSal [5,27–31]. In this study, 3C12trisQ aggregates in solution also changed from spherical to rodlike micelles in the $C_S/C_D$ range of 0.24–0.30. On the other hand, for $0.45 \leq C_S/C_D \leq 0.66$, the viscosity was a monotonic function of shear rate. This is a well-known phenomenon, called “shear thinning”, and indicates the formation of wormlike micelles [5,14,31,32]. Therefore, in the $C_S/C_D$ range from 0.45 to 0.66, wormlike micelles formed by 3C12trisQ in solution grew with increasing NaSal concentration. Interestingly, the viscosity dramatically decreased at $C_S/C_D = 0.8$ and became similar to that of water. Similar rheological behavior was observed in a cationic monomeric surfactant solution containing 5-methylsalicylic acids, and it was suggested that the decrease in viscosity was due to a micelle-to-vesicle transition [33]. In the present study, the SAXS results suggested that 3C12trisQ forms MLVs in solution, as indicated in Figure 4.

Figure 2b shows the rheological behavior of 3C12trisQ solutions at $C_D = 14$ mM with $C_S/C_D$ ratios ranging from 0 to 0.2. At $C_S/C_D = 0$, the viscosity was higher than that of water and was independent of the share rate, similar to the 3C12trisQ solution at $C_D = 7$ mM and $C_S/C_D = 0.3$. This indicates that 3C12trisQ ($C_D = 14$ mM) formed rodlike micelles in solution, even at $C_S/C_D = 0$. As the $C_S/C_D$ increased from 0 to 0.045, the viscosity gradually increased while remaining independent of the share rate. When the $C_S/C_D$ ratio was increased further, share thinning was observed for $0.06 \leq C_S/C_D \leq 0.2$. We found that 3C12trisQ ($C_D = 14$ mM) formed rodlike micelles in solution at $C_S/C_D = 0,$
and the rodlike micelles became longer with increasing $C_S/C_D$ ratio from 0 to 0.2. In Figure 2c, for $C_D = 28$ mM, shear-thinning behaviors were observed at all $C_S/C_D$ ratios, indicating that 3C$_{12}$trisQ formed entangled wormlike micelles in this $C_S/C_D$-range.

Figure 3 shows the $C_S/C_D$-dependence of zero-shear viscosity ($\eta_0$) estimated from the shear-rate dependence of the viscosity of 3C$_{12}$trisQ solutions. At $C_S/C_D = 0$, comparing with the $\eta_0$ value of water, the $\eta_0$ value of 3C$_{12}$trisQ solutions at $C_D = 7$ mM was same, whereas ones at $C_D = 14$ and 28 mM were higher. The increase in the $\eta_0$ value was due to formation of rodlike micelles. Furthermore, the $\eta_0$ values drastically increased at $0.3 \leq C_S/C_D \leq 0.66$ for $C_D = 7$ mM, and all the NaSal concentration for $C_D$ 14 and 28 mM, which also clearly indicated the wormlike micellar growth by increasing $C_S/C_D$ ratio.

Based on the rheological measurements, the aggregation behavior of 3C$_{12}$trisQ at different surfactant concentrations and $C_S/C_D$ ratios is summarized as follows. The 3C$_{12}$trisQ micelles in solution at $C_D = 7$ mM exhibited sphere-to-rod transitions and

**Figure 3.** $C_S/C_D$ dependence of the zero-viscosity ($\eta_0$) estimated from the shear-rate dependence of the viscosity of 3C$_{12}$trisQ solutions.
micelle-to-vesicle transitions with increasing NaSal concentration. At higher sample concentrations (C_D =14 and 28 mM), wormlike micelles were formed, even in the salt-free condition, and grew into entangled wormlike micelles with increasing NaSal concentration. However, we did not observe vesicle formations of 3C_{12}trisQ in solution at C_D =14 and 28 mM because 3C_{12}trisQ were insoluble in solution above the NaSal solubility-limit concentration. Therefore, the rheological measurements suggested that the wormlike micelle-to-vesicle transitions of 3C_{12}trisQ were observed exclusively at low surfactant concentration (i.e., C_D = 7 mM).

3.2. NaSal concentration dependence of 3C_{12}trisQ aggregates in solutions at low surfactant concentration (7 mM)

In the previous subsection, we found that 3C_{12}trisQ (C_D = 7 mM) formed four aggregate structures in solutions depending on the C_S/C_D ratio: (i) spherical (ellipsoidal) micelles in C_S/C_D ≤ 0.24, (ii) rodlike micelles at C_S/C_D = 0.3, (iii) wormlike micelles in 0.45 ≤ C_S/C_D ≤ 0.66, and (iv) vesicles at C_S/C_D = 0.8. In this subsection, SAXS measurements were carried out to study the C_S/C_D-dependence of 3C_{12}trisQ solutions at C_D = 7 mM to quantitatively reveal the 3C_{12}trisQ aggregates.

3.2.1. SAXS results

Figure 4 shows the SAXS profiles of 3C_{12}trisQ in solution at C_D = 7 mM at different C_S/C_D-ratios. With the exception of C_S/C_D = 0.8, the SAXS profiles of the 3C_{12}trisQ solutions displayed two broad peaks at q ~ 0.03 Å\(^{-1}\) and q ~ 0.2 Å\(^{-1}\), reflecting the inter- and intra-micellar structures, respectively. The peak in the higher
The broad peak in the lower $q$-range of $q \sim 0.01-0.03$ Å$^{-1}$ was attributed to electrostatic repulsion between the micelle surface charges. By increasing the $C_S/C_D$ ratio in the measured $C_S/C_D$ range.
ratio, the peak position ($q_{m1}$) in the lower $q$ region changed monotonically. Figure 5a shows the $C_S/C_D$ dependence of $q_{m1}$ in the $q$ range of $q \sim 0.01$–0.03 Å$^{-1}$. Previously, for salt-free cationic surfactant solutions, we found a correlation between $q_{m1}$ behavior and the $\eta_0$ value obtained from the shear-rate dependence of viscosity [14]. Here, Figure 5b shows the $C_S/C_D$ dependence of the $\eta_0$ values for $C_D = 7$ mM, which is same the result (green rectangle) plotted in Figure 3. We can confirm that the $\eta_0$ was strongly correlated to $q_{m1}$. As the $C_S/C_D$ ratio increased from 0 to 0.24, $q_{m1}$ shifted downward from 0.0247 to 0.017 Å$^{-1}$; however, it remained constant for $C_S/C_D$ ratios between 0.30 and 0.66.

When the $C_S/C_D$ ratio was further increased to 0.8 (Figure 4), the peak ($q_{m1}$) in the
A range of \( q \approx 0.01–0.03 \text{ Å}^{-1} \) disappeared and the SAXS profile displayed an asymptotic \( q^{-2} \) behavior in the \( q \) range of \( q \leq 0.03 \text{ Å}^{-1} \). Simultaneously, a sharp peak \( (q_{m3}) \) appeared in the SAXS profile at \( q = 0.19 \text{ Å}^{-1} \). In addition, we found that the \( \eta_0 \) value dramatically decreased at \( C_S/C_D = 0.8 \) (Figure 5b). The SAXS and \( \eta_0 \) results indicate that 3C\(_{12}\)trisQ formed MLVs at \( C_S/C_D = 0.8 \). Similarly, MLV formation was also observed in 12-2-12(Et) by the addition of NaSal [7]. Note that monomeric cationic surfactants with the same hydrocarbon chain length (\( n = 12 \)) form no vesicles in solution.

### 3.2.2. Model-fitting analysis of SAXS results

To determine the structural parameters of 3C\(_{12}\)trisQ aggregates in solution, we performed model-fitting analyses on the SAXS results. Here, we discuss the aggregation behavior of 3C\(_{12}\)trisQ during the sphere-to-rod transition of micelles. For \( C_S/C_D \leq 0.24 \), 3C\(_{12}\)trisQ aggregates were found to be spherical (ellipsoidal) micelles in solution. For the model-fitting analyses, we adopted a charged core-shell ellipsoid model, whose theoretical scattering curve was evaluated by equations (2)–(4). Because 3C\(_{12}\)trisQ formed rodlike micelles in solutions with \( C_S/C_D = 0.3 \), a charged core-shell cylindrical model described by equations (5)–(7) was employed for the analysis. Note that the scattering contrast of the core portion was fixed in all model-fitting analyses.

For \( 0.45 \leq C_S/C_D \leq 0.66 \), the wormlike micelles formed by 3C\(_{12}\)trisQ cannot be analyzed by the charged core-shell ellipsoid model because the structural factors \( S(q) \) corresponding to the peak profile in the lower \( q \) region remain unsolved. The Hayter–Penfold structure factor \( S_{HP}(q) \) was employed in the analysis of rodlike micelles.
However, if the micellar length $L$ is much larger than the cross-sectional radius $R_C$ (i.e. $L >> R_C$), $S_{HP}(q)$ cannot be used for model fitting. An alternative model, a PRISM structure factor $S_{PRISM}(q)$, has been proposed for monomeric cationic surfactant solutions with high salt concentrations [36]. However, the SAXS results of 3C$_{12}$trisQ solutions cannot be fitted by a theoretical scattering using $S_{PRISM}(q)$ with the form factor of a rod particle model. Therefore, in the present study, we did not perform any model-fitting analysis for $0.45 \leq C_S/C_D \leq 0.66$. The occurrence of overlapping wormlike micelles requires further investigation using other techniques such as cryo-TEM observations.

Figure 6 shows the best-fitted theoretical scattering curves with experimental SAXS profiles for 3C$_{12}$trisQ aggregates. In the higher $q$-region, the theoretical scattering curves did not agree with the experimental results. This discrepancy was due to the following assumptions: (1) the scattering length densities in both the shell and core portions are homogeneous, (2) the interface between the shell and core portions within the inner core-shell particle models is sharp [37], and (3) the core radius is monodispersed. The effect of the dispersity in the core radius on the theoretical scattering curve was discussed in detail [38]. For $C_S/C_D = 0.3$, the disagreement with the experimental results in the $q$ range of $q \sim 0.07$–$0.1$ Å$^{-1}$ (as marked by the arrow in Figure 6) is probably due to the assumption of a monodispersed cylinder. However, the observed SAXS profiles were successfully fitted with theoretical scattering curves for $q \leq 0.06$ and $q \sim 0.1$–$0.3$ Å$^{-1}$, reflecting a micellar shape, size, internal structure, and inter-particle distance.
Table 1 and Figures 7a–d show the structural parameters obtained from the model-fitting analysis of the SAXS profiles. Both shell thickness ($T_s$; Figure 7a) and core radius ($R_c$; Figure 7b) show no change in the $C_S/C_D$ range of $0 \leq C_S/C_D \leq 0.3$, and the mean values are $\bar{T}_s = 4.9$ Å and $\bar{R}_c = 15.0$ Å. The axial ratio ($\nu_c$; Figure 7b) gradually grew from 3.82 to 6.69 by increasing the $C_S/C_D$ ratio from 0 to 0.24. These results indicate that by increasing the NaSal concentration, the micellar structures became longer by maintaining the cross-sectional radius. This behavior is similar to the

**Figure 6.** Comparisons of fitted theoretical scattering curves (solid and dashed lines) and experimental results (symbols) for the 3C$_{12}$trisQ solutions. The solid and dashed lines were evaluated using a charged core-shell ellipsoid model and a charged core-shell cylinder model, respectively. The profiles are vertically shifted to avoid overlap.
CD dependence of 3C12trisQ aggregates under salt-free conditions [14]. For CS/CD = 0.3, the apparent core-axial ratio (uc^cyt) of rodlike micelles was estimated to be uc^cyt = 12.4 by (Lc/2)/Rc with Lc = 365.1 Å and Rc = 14.7 Å (where Lc is the total core length). The uc^cyt value for CS/CD = 0.3 was much larger than the uc value for CS/CD = 0.24. When 3C12trisQ aggregates transformed from ellipsoidal micelles to rodlike ones, the micellar length drastically increased. With increasing the CS/CD ratio, the surface charge was clearly decreased because of the screening of electrostatic repulsions between micelles.

On the other hand, the Debye length (ld) linearly increased at the CS/CD ratio of 0–0.24 and drastically increased with increasing CS/CD ratio from 0.24 to 0.3 (Figure 7c). This behavior was related to an increase in aggregate length with the addition of NaSal.

The scattering contrast (Δρs) of the shell portion linearly increased from 2.48 × 10⁻⁶ Å⁻² to 2.95 × 10⁻⁶ Å⁻² when the CS/CD ratio was increased from 0.0 to 0.3 (Figure 7d). We can deduce that the shell portion was composed of three factors: the hydrophilic

| Table 1. Structural parameters for 3C12trisQ (CD = 7 mM) in solution with NaSal. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| CS/CD | Micellar shape | Rc (Å) | Ts (Å) | uc (–) | ld (Å) | Δρs (10⁻⁶ Å⁻²) |
| 0    | Ellipsoidal micelles | 14.9 | 4.94 | 3.82 | 75.7 | 2.48 |
| 0.03 |                 | 14.9 | 4.86 | 4.42 | 77.4 | 2.59 |
| 0.09 |                 | 14.9 | 4.95 | 5.83 | 78.66 | 2.61 |
| 0.18 |                 | 15.2 | 4.83 | 6.24 | 91.90 | 2.76 |
| 0.24 |                 | 15.4 | 4.85 | 6.69 | 109.48 | 2.81 |

Rc (Å): The radius for ellipsoidal model and cross-sectional radius for rod model. Ts (Å): The shell-thickness. uc: The axial ratio. ld: The Debye length. Δρs: The scattering contrast of the shell portion. Lc: The core length for rod.
head groups of the 3C_{12}\text{trisQ} molecule, the penetrated water, and the added NaSal. Regarding the increase in $\Delta \rho_s$, we deduce that the exclusion of water from the hydrophilic shell portion and/or the penetration of NaSal into the micelles contributed to the increased $\Delta \rho_s$ because the scattering length densities of both hydrophilic head groups and NaSal are higher than that of water.
Figure 7. $C_S/C_D$ dependence of the structural parameters determined by model-fitting analysis of the SAXS results: (a) shell thickness ($T_s$); (b) core radius ($R_c$) and axial ratio ($\mu_c$) of the core portion; (c) Debye length ($\lambda_D$); and (d) scattering contrast of the shell portion ($\Delta\rho_s$), respectively.
3.2.3. Sphere-to-rod transition of $3C_{12}$trisQ micelles in solutions containing NaSal

In this subsection, we discuss the NaSal-induced a sphere-to-rod transition of $3C_{12}$trisQ micelles in solution based on the structural parameters obtained by the model-fitting analysis. First, we should mention the well-known critical packing parameter (CPP) consideration proposed by Israelachvili [39]. The CPP is given by

$$CPP = \frac{v_{\text{tail}}}{a_0 l_c}$$  \hspace{1cm} (11)

where $v_{\text{tail}}$, $a_0$, and $l_c$ are the volume of the hydrocarbon chains, optical area of the hydrophilic head, and length of the critical hydrocarbon chain, respectively. For spherical micelles, CPP < 1/3, while for rodlike micelles, 1/3 < CPP < 1/2. We estimated the CPP of the $3C_{12}$trisQ solution with $C_D = 7$mM from the results of the model-fitting analysis. In equation (11), $v_{\text{tail}}$ and $a_0$ are, respectively, given by

$$v_{\text{tail}} = \frac{V_{\text{core}}}{N_{\text{agg}}}$$  \hspace{1cm} (12)

and

$$a_0 = \frac{A_{\text{micelle}}}{N_{\text{agg}}}$$  \hspace{1cm} (13)

where $V_{\text{core}}$, $A_{\text{micelle}}$, and $N_{\text{agg}}$ are the volume of the core portion, the area of the micelles, and the aggregation number, respectively. We regarded the core radius ($R_c$) as $l_c$ in equation (11). Using equations (11)–(13), the CPP can then be written as

$$CPP = \frac{V_{\text{core}}}{(A_{\text{micelle}} R_c)}$$  \hspace{1cm} (14)

The values of both $V_{\text{core}}$ and $A_{\text{micelle}}$ were estimated from the results of model-fitting analysis. The estimated CPP values of $3C_{12}$trisQ aggregates are shown in Table 2. When $C_S/C_D$ was increased further from 0.24 to 0.3, the CPP of the $3C_{12}$trisQ aggregates
became larger than 1/3, indicating that the behavior of the SAXS profile of the 3C\textsubscript{12}trisQ solution at $C_D = 7$ mM is consistent with the CPP considerations.

As the $C_S/C_D$ ratio increased from 0 to 0.24, the CPP gradually increased from 0.282 to 0.305. According to the results of the model-fitting analysis, the axial ratio of the core portion gradually increased, while the core radius remained constant. This change was accompanied by an increase in the scattering contrast of the shell portion due to the penetrations of NaSal and exclusion of water from the shell portion. The existence of NaSal molecules in the inner shell portion changed the surface to volume ratio of the micelles, and increased the membrane curvatures of the micelles, leading to the large CPP.

On the other hand, when the $C_S/C_D$ ratio was increased from 0.24 to 0.3, the 3C\textsubscript{12}trisQ micelles underwent sphere-to-rod transitions and the micellar length drastically increased. In the case of the transitions induced by increasing the surfactant concentration under salt-free conditions, the lengths of rodlike micelles gradually increased during the transitions [14], which was marked different than the observed NaSal-induced transitions. Here, we discussed the micellar growth of 3C\textsubscript{12}trisQ aggregates. For micelles screened by electrostatic repulsion, the average contour length

<table>
<thead>
<tr>
<th>$C_S/C_D$ ratio</th>
<th>0</th>
<th>0.03</th>
<th>0.09</th>
<th>0.18</th>
<th>0.24</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CPP$</td>
<td>0.282</td>
<td>0.290</td>
<td>0.297</td>
<td>0.303</td>
<td>0.305</td>
<td>0.348</td>
</tr>
</tbody>
</table>
(L_{av}) is given by [40]

\[ L_{av} \sim \phi^{1/2} \exp\left((E_c - E_e)/2k_B T\right) \tag{15} \]

where \( \phi, T, E_c, \) and \( E_e \) are the surfactant volume fraction, the temperature, the end-cap energy, and the electrostatic contribution, respectively. \( E_e \) is given by

\[ E_e \sim k_B T l_B R_a \alpha^2 \phi^{1/2} \tag{16} \]

where \( l_B, R_a, \) and \( \alpha \) are the Bjerrum length, the cross-section radius of the rodlike micelles, and effective charge per unit length, respectively. Decreases in \( \alpha \) lead to increases in \( L_{av} \). Therefore, it is deduced that this large decrease in the surface charge reduced the \( E_e \) contribution for the rodlike micelles and resulted in the drastic elongation of the rodlike micelles.

### 3.3. Comparison of multi-lamellar vesicles formed by 3C_{12}trisQ and gemini-type surfactant (12-2-12) in solutions containing NaSal

As shown in Figure 4, we found that a 3C_{12}trisQ solution with \( C_D = 7 \) mM exhibited transitions from wormlike micelles to MLVs when the NaSal concentration was increased. Previously, it was previously reported that 12-2-12(Et) aggregates formed vesicles [7]. As with a sphere-to-rod transition, the micelle-to-vesicles transition can be explained by consideration of CPP theory. Both introducing spacer chains and electrostatic screening of cationic surfactant increase CPP of the cationic surfactant aggregates. Here, by comparing the MLVs formed by 3C_{12}trisQ with those formed in 12-2-12 solutions containing NaSal, we discuss the effect of introducing spacer chains on the structural properties of MLVs.
Figure 8 shows the SAXS profiles of 3C_{12}trisQ and 12-2-12 solutions with the same surfactant volume fraction ($\phi_D = 0.007$) containing NaSal. This volume fraction corresponds to $C_D = 7$ mM for 3C_{12}trisQ and $C_D = 11$ mM for 12-2-12. The NaSal concentrations were $C_S = 5.5$ mM for 3C_{12}trisQ solution and $C_S = 10.6$ mM for 12-2-12 solution. Sharp peaks appeared in the SAXS profiles at $q_{m3} = 0.19$ Å$^{-1}$ for the 3C_{12}trisQ solution and at $q_{m3} = 0.28$ Å$^{-1}$ for the 12-2-12 solution. The repeat distance ($d$) of 12-2-12 was estimated to be 22.36 Å. Note that the hydrocarbon chain length was the same for both 3C_{12}trisQ and 12-2-12. In fact, both SAXS profiles exhibited a broad peak at around $q = 0.2$ Å$^{-1}$, which qualitatively suggests that the membrane thicknesses of the 3C_{12}trisQ vesicles are almost the same as those of the 12-2-12 vesicles. On the

![Figure 8](image)

**Figure 8.** SAXS profiles of star-type trimeric surfactants (3C_{12}trisQ) and gemini-type cationic surfactants (12-2-12) in solutions containing NaSal at the same volume fraction ($\phi_D$). The NaSal concentrations ($C_S$) were 5.5 mM for 3C_{12}trisQ solution and 6.4 mM for 12-2-12 solution.
other hand, the $d$ value of the 3C$_{12}$trisQ solution ($d = 33.05 \, \text{Å}$), described in subsection 3.2, was remarkably larger than that of the 12-2-12 one. The difference in $d$ value was attributed to the differences between the 3C$_{12}$trisQ and 12-2-12 membranes.

Micelle-to-vesicle transitions were attributed to the electrostatic screening of cationic surfactant solutions by the addition of NaSal. The difference in distance between the membranes of 3C$_{12}$trisQ and 12-2-12 appeared to be directly related to the NaSal concentration at which the micelle-to-vesicles transitions occurred. Here, we estimated the molar ratio ($R_M$) of NaSal to monomeric chain ($n_c$) of surfactants by $R_M = \frac{C_S}{(n_c C_D)}$ (where $n_c$ is 3 for 3C$_{12}$trisQ and 2 for 12-2-12); the $R_M$ values were estimated to be 0.266 for 3C$_{12}$trisQ and 0.477 for 12-2-12. This suggests that the repeat distance of 3C$_{12}$trisQ aggregates is larger than that of the 12-2-12 because of strong electrostatic repulsion. This difference in the repeat distance is also related to the presence of spacer chains. Increasing the number of spacer chains leads to a decrease in the membrane curvature. Therefore, 3C$_{12}$trisQ could potentially form vesicular structures at a lower NaSal concentration compared to 12-2-12. In fact, the monomeric surfactant did not form any MLV membrane regardless of the relative salt concentration. Therefore, we found that introducing spacer chains helped to decrease the NaSal concentrations observed in the micelle-to-vesicles transitions; in turn, this effect caused the difference in MLV membrane distance between 3C$_{12}$trisQ and 12-2-12.
4. Conclusions

We investigated the structural transitions of aggregates of star-type trimeric surfactants (3C_{12}trisQ) in solutions containing sodium salicylate (NaSal) using small-angle X-ray scattering (SAXS) and rheological measurements. The 3C_{12}trisQ solution with \( C_D = 7 \text{ mM} \) underwent a structural transition from ellipsoidal micelles to multi-lamellar vesicles (MLVs) through rodlike and wormlike micelles as the NaSal concentration increased. This aggregate growth was attributed to not only the electrostatic screening of NaSal molecules but also the exclusion of water from the inner micelles by the penetration of NaSal into the micelles. As reported in our previous study, spacer chains of 3C_{12}trisQ induced the sphere-to-rod transitions of micelles by increasing the end-cap energy of wormlike micelles, resulting in the sphere-to-rod transitions at lower salt and surfactant concentrations [14]. In addition, we found that the spacer chains of 3C_{12}trisQ also induced micelle-to-MLV transitions. In contrast, at higher surfactant concentrations (\( C_D = 14 \) and 28 mM), no vesicles were formed by 3C_{12}trisQ. The MLV structure formed by 3C_{12}trisQ (\( C_D = 7 \text{ mM} \)) was compared with that formed by gemini-type surfactants (12-2-12). The estimated repeat distance of the 3C_{12}trisQ was larger than that of the 12-2-12. Furthermore, we also found that introducing spacer chains decreased in NaSal concentrations at which micelle-to-vesicle transitions were caused because membrane curvature was decreased.
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Structural Study on Aggregation Behavior of Star-Type Trimeric Surfactant in the Presence of Sodium Salicylate

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