Solution Properties of Dissymmetric Sulfonate-type Anionic Gemini Surfactants

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Abstract: Dissymmetric and symmetric anionic gemini surfactants, N-alkyl-N’-alkyl-N,N’-dipropanesulfonylethylenediamine (CₘCₙSul, where m and n represent alkyl chain lengths of m-n = 4-16, 6-14, 8-12, 10-10, and 12-12), were synthesized by two- or three-step reactions. Their physicochemical properties were characterized by equilibrium surface tension measurements, steady-state fluorescence spectroscopy of pyrene, and dynamic light scattering. The critical micelle concentration (CMC) of the dissymmetric surfactants C₈C₆Sul, C₆C₄Sul, and C₄C₂Sul was slightly lower than that of the symmetric surfactant C₁₀C₈Sul. The occupied area per molecule (A) of C₈C₆Sul was smaller than that of C₁₀C₈Sul, indicating that C₈C₆Sul has a high surface activity. However, the increase in the degree of dissymmetry from C₈C₆Sul to C₆C₄Sul and then to C₄C₂Sul resulted in high surface tension and large A. Based on the surface tension, the standard free energies of micellization (ΔGmic) and adsorption (ΔGads), the efficiency of surface adsorption (pCₙ), and the effectiveness of surface adsorption (CMC/Cₚ) were obtained. These parameters suggested that C₈C₆Sul formed micelles more readily than the other surfactants. The properties determined from the surface tension indicated that C₈C₆Sul’s ability is intermediate between those of C₁₀C₈Sul and C₆C₄Sul. The pyrene fluorescence and dynamic light scattering results revealed that the micelle size depends on the longer of the two alkyl chains in dissymmetric surfactants.

Key words: gemini surfactant, anionic surfactant, dissymmetric gemini, solution property, micelle

1 INTRODUCTION

Gemini surfactants are composed of two hydrophilic groups and two hydrophobic chains linked by a spacer at the level of the molecules’ head groups. Compared with their monomeric surfactant counterparts, gemini surfactants exhibit very low critical micelle concentrations (CMC), are highly efficient at lowering the surface tension, have good solubility in water, have low Krafft temperatures, and exhibit strong interactions with oppositely charged surfactants at the air/water interface. They are widely used as detergents, emulsifiers, and dispersants, as well as in other applications. Various types of gemini surfactants have been investigated; for example, researchers have experimented with varying the spacer’s structure from hydrophilic to hydrophobic and from flexible to rigid. In recent years, new types of gemini surfactants with non-symmetrical structures have emerged and attracted substantial attention. Two types of such surfactants exist: asymmetric gemini surfactants with two identical alkyl chains and two different hydrophilic head groups, and dissymmetric ones with two different alkyl chain lengths and two identical head groups. The latter were studied by Oda and co-workers in 1997 for the first time. Those researchers synthesized the cationic dissymmetric surfactants [CₘH₂ₙ₊₁(CH₂)ₙ-N’-(CH₂)ₙ-N(CH₂)ₙCₙH₂ₙ₊₁]Br₂, designated Cₘ₋ₙCₙBr₂, and reported that these surfactants produce very interesting micelle shapes in aqueous solution. Sikirić et al. investigated the effect of spacer length on dissymmetric surfactants and found that the Krafft temperature increases linearly with spacer length and that both adsorption at the air/water interface and micellization in aqueous solution are heavily dependent on the spacer length. Yan et al. synthesized Cₘ₋ₙCₙBr₂ with m + n = 24, where m = 12, 13, 14, 16, or 18, and found that, as the m:n ratio was increased, the surface activities improved, the CMC values decreased linearly, and the aggregation numbers at the CMC increased slightly. These studies investigating dissymmetric surfactants focused on the choice of whether to fix the total carbon numbers of the hydrocarbon chains and their spacers or not. Further-
more, regarding studies in which the total numbers of the hydrophobic alkyl chains are fixed, surfactants with both small and large degrees of dissymmetry have been characterized. As the degree of dissymmetry \( m/n \) increases, the structure of the dissymmetric gemini surfactants becomes increasingly similar to that of surfactants with one hydrocarbon chain and two hydrophilic head groups. In contrast, the structures of dissymmetric gemini surfactants with small degrees of dissymmetry are more similar to those of symmetric gemini surfactants. Thus, changing the degree of dissymmetry in the hydrocarbon chains is expected to result in different surface-active properties from those of conventional surfactants, and thus, this topic has attracted substantial amounts of attention. The dissymmetric gemini surfactants reported to date include quaternary ammonium salts in their hydrophilic head groups. Currently, there are no reports of dissymmetric anionic gemini surfactants and the surface properties of dissymmetric cationic ones.

In this study, we synthesized the dissymmetric anionic gemini surfactants \( N\)-alkyl-\( N'\)-alkyl-\( N'\)-dipropanesulfonylethylene diamine (\( C_mC_n\text{Sul} \), \( m-n = 4-16, 6-14, 8-12, 10-10, 12-12 \)) and characterized their aqueous solution properties by measuring the surface tension and analyzing pyrene fluorescence spectra and dynamic light scattering results. The chemical structure of \( C_mC_n\text{Sul} \) is shown in Fig. 1.

### 2 EXPERIMENTAL

#### 2.1 Materials

Ethylene diamine, methanol, ethanol, acetone, diethyl ether, 1, 4-dioxane, and ethyl acetate were obtained from Kanto Chemicals Co., Inc. (Tokyo, Japan) and used without further purification. 1-Butyl bromide, 1-hexyl bromide, 1-octyl bromide, 1-decyl bromide, 1-dodecyl bromide, 1-tetradecyl bromide 1-octadecyl bromide, and 1,3-propanesultone were purchased from Tokyo Kasei Co., Ltd. (Tokyo, Japan).

#### 2.2 Synthesis

**2.2.1 \( N\)-Alkylethylenediamine (\( C_m \))**

First, 5.0 eq of 1-dodecyl, 1-tetradecyl-, or 1-octadecyl bromide was added dropwise to ethylene diamine dissolved in ethanol, and the mixture was then refluxed at 78°C for 24 h under alkaline conditions produced by adding NaOH with thymolphthalein as an indicator. The mixture was filtered to remove the inorganic salt that formed (\( \text{NaBr} \)) and evaporated to remove the solvent. The residue was washed with 0.1-M NaOH solution and poured into a separatory funnel with diethyl ether. Hydrochloride gas was added to the organic layer to give \( N\)-alkylethylenediamine hydrochloride (\( C_m\text{HCl} \)) as a white solid. This solid was heated in methanol, and then, the undissolved white solid, which was the compound with two alkyl chains (\( N, N'\)-dialkylethylene diamine hydrochloride (\( 2C_m\text{HCl} \)) was filtered out. As the methanol cooled, a white solid, which was the compound with one alkyl chain (\( C_m\text{HCl} \)), precipitated. This solid was recrystallized several times from methanol, and dried under reduced pressure. The structures were confirmed by \( ^1\text{H} \) NMR (JEOL JNM-EX 500) and elemental analysis (Perkin Elmer 2400II CHNS/O).

**2.2.2 \( N\)-Alkyl-\( N'\)-alkylethylenediamine (\( C_mC_n \))**

First, 0.1-M NaOH solution was added to dissolve the undissolved \( C_m\text{HCl} \) in methanol by removing HCl from \( C_m\text{HCl} \), yielding \( C_m \). Then, 1.5 eq of 1-octyl, 1-hexyl-, or 1-butyl bromide was added dropwise to the \( C_m \) dissolved in methanol, and the reaction was refluxed at 64°C for 48 h under alkaline conditions obtained by adding NaOH with thymolphthalein as an indicator. The mixture was filtered to remove the inorganic salt that formed (\( \text{NaBr} \)) and the filtrate was evaporated under reduced pressure. The residue was washed with 0.1-M NaOH solution and poured into a separatory funnel with diethyl ether. Hydrochloride gas was added to the organic layer to obtain \( N\)-alkyl-\( N'\)-alkylethylenediamine hydrochloride (\( C_mC_n\text{HCl} \)) as a white solid, which was recrystallized several times from methanol, and dried under reduced pressure. The structures were confirmed by \( ^1\text{H} \) NMR and elemental analysis.

NaOH solution adjusted to pH 12–13 was added dropwise to \( C_mC_n\text{HCl} \) in heated 1,4-dioxane to remove HCl, yielding a clear solution. After cooling the solution to room temperature, the mixture was poured into a separatory funnel. The upper layer was evaporated to remove the solvent. The residue was recrystallized several times from ethyl acetate and dried under reduced pressure, giving \( N\)-alkyl-\( N'\)-alkylethylenediamine (\( C_mC_n \)) as a white solid.
2.2.3 N,N'-Dialkylethlenediamine (C₄₈N₄)

First, 2.2 eq of 1-decyl or 1-dodecyl bromide was added dropwise to ethylenediamine dissolved in ethanol, and then, the reaction was refluxed at 78°C for 24 h under alkaline conditions achieved by adding NaOH with thymol as an indicator. The processes used for the purification of and HCl removal from C₄₈N₄HCl were the same as those used for C₄₈N₄. The structures of C₄₈N₄ were confirmed by ¹H NMR and elemental analysis.

2.2.4 N-Alkyl- N'-alkyl-N,N'-dipropanesulfonylethlenedi- amine (C₄₈N₄Sul) and N,N'-dialkyl-N,N'-dipropanesul- fonylethlenediamine (C₄₈N₄Sul)

First, 3.0 eq of 1,3-propanesultone was added dropwise to C₄₈N₄ or C₄₈N₄ dissolved in acetone, and then, the reaction was refluxed at 56°C for 48 h. After cooling the mixture to room temperature, it was filtered to obtain N,N′-dialkyl-N,N′-dipropanesulfonylethlenediamine (C₄₈N₄Sul) or N,N′-dialkyl-N,N′-dipropanesulfonylethlenediamine (C₄₈N₄Sul) as white solids. The C₄₈N₄Sul or C₄₈N₄Sul obtained was washed several times with ethyl acetate followed by acetone and recrystallized from mixtures of methanol and water. The structures of C₄₈N₄Sul and C₄₈N₄Sul were confirmed by ¹H NMR and elemental analysis. ¹H NMR (CD₂OD, NaOD): C₄₈N₄Sul. δ 8.55–1.00 (6H, CH₂–CH₂–), 1.23–1.42 (28H, CH₃–CH₂–CH₂–, CH₃–(CH₂)₉–CH₂–), 1.52 (4H, –CH₂CH₂CH₂CH₂–N–, –(CH₂)₉–CH₂–CH₂–N–), 1.96 (4H, –CH₂CH₂CH₂CH₂–N–, –(CH₂)₉–CH₂–CH₂–N–), 2.43–2.71 (12H, –N–(CH₂)₉–SO₃H), 2.90 ppm (4H, –N–(CH₂)₉–N–). C₄₈N₄Sul. δ 6.85–0.99 (6H, CH₃–CH₂–), 1.22–1.42 (28H, CH₃–(CH₂)₉–CH₂–, CH₃–(CH₂)₉–CH₂–), 1.52 (4H, –CH₂–CH₃–CH₂–CH₂–N–, –(CH₂)₉–CH₂–CH₂–N–), 1.94 (4H, –(CH₂)₉–CH₂–CH₂–N–, –(CH₂)₉–CH₂–CH₂–N–), 2.43–2.70 (12H, –N–(CH₂)₉–SO₃H), 2.88 ppm (4H, –N–(CH₂)₉–N–). C₄₈N₄Sul. δ 0.90–6.00 (6H, CH₃–CH₂–), 1.22–1.42 (28H, CH₃–(CH₂)₉–CH₂–), 1.52 (4H, –(CH₂)₉–CH₂–CH₂–N–, 1.95 (4H, –CH₂–CH₂–CH₂–N–), 2.45–2.70 (12H, –N–(CH₂)₉–SO₃H), 2.87 ppm (4H, –N–(CH₂)₉–N–). Elemental analysis: C₄₈N₄Sul. Calcd for C₂₈H₅₀N₄O₆S₂: C, 55.78; H, 10.37; N, 4.65. Found: C, 56.00; H, 10.43; N, 4.63. C₄₈N₄Sul. Calcd for C₂₈H₅₀N₄O₆S₂·0.5H₂O: C, 56.62; H, 10.35; N, 4.72. Found: C, 56.22; H, 10.65; N, 4.69. C₄₈N₄Sul. Calcd for C₂₈H₅₀N₄O₆S₂·H₂O: C, 55.78; H, 10.37; N, 4.65. Found: C, 56.00; H, 10.80; N, 4.65. C₄₈N₄Sul. Calcd for C₂₈H₅₀N₄O₆S₂·C, 57.50; H, 10.34; N, 4.79. Found: C, 57.29; H, 10.32; N, 4.74. C₄₈N₄Sul. Calcd for C₂₈H₅₀N₄O₆S₂·C, 59.96; H, 10.69; N, 4.37. Found:

C, 59.66; H, 10.80; N, 4.34.

2.3 Measurements

The disymmetric and symmetric anionic gemini surfactant (C₄₈C₄₈Sul and C₄₈C₄₈Sul) solutions were adjusted to pH 13 with 0.1-M NaOH, and the measurements were performed at 25 ± 0.5°C.

2.3.1 Methods for determining general properties

The surface tensions of aqueous solutions of the disymmetric and symmetric anionic gemini surfactants C₄₈C₄₈Sul and C₄₈C₄₈Sul were measured with a Kruess K100 tensiometer using the Wilhelmy plate technique. The surface excess concentration (Γ) in mol m⁻² and the area occupied by each molecule (A) of each anionic surfactant at the air/solution interface were calculated using the classic Gibbs adsorption isotherm equations: Γ = - (1/2RT) (dp/dlnC) and A = 1/(NΓ). Here, γ is the surface tension; C, the surfactant concentration; R, the gas constant (8.31 J K⁻¹ mol⁻¹); T, the absolute temperature; and N, Avogadro’s number. The value of i in the equation for a dilute solution of a gemini surfactant at pH 13 is taken to be 1, which is the number of possible species. The fluorescence measurements of the gemini surfactants C₄₈C₄₈Sul and C₄₈C₄₈Sul were performed with a Hitachi 650-108 fluorescence spectrophotometer. The DLS measurements were performed with a DLS-7000 instrument (Otsuka Electronics Co., Ltd., Japan) with an Ar laser (λ = 488 nm) at a scattering angle of 90°. For spherical particles, the diffusion coefficient extrapolated to zero concentration (D₀) can be converted to the apparent hydrodynamic diameter (Dₚ) using the Stokes–Einstein relation: D₀ = kT/6πηDₚ. Here, k is the Boltzmann constant; T, the absolute temperature; and η, the viscosity of the solution.

3 RESULTS AND DISCUSSION

3.1 Surface tension properties

The equilibrium surface tension values as functions of the surfactant concentrations of C₄₈C₄₈Sul, C₄₈C₄₈Sul, C₄₈C₄₈Sul, C₄₈C₄₈Sul, and C₄₈C₄₈Sul are shown in Fig. 2. The surface tensions decrease as the concentrations increase and then reach clear break points, which are taken as the CMCs. The values of the CMC, surface tension at the CMC (γCMC), Γ, and A, are shown in Table 1. Here, Cₘ₀ is the concentration that reduces the surface tension of water by 52 mN m⁻¹. The CMCs of conventional ionic surfactants are known to decrease as the number of carbon atoms in the hydrophobic groups increase to approximately up to approximately 16 (a hexadecyl group). Gemini surfactants are known to show low CMCs compared with monomeric surfactants because of their strong hydrophobic interactions. Accordingly, the increase in the number of carbon atoms in the
hydrophobic groups has an influence on the CMC equivalent to that of the loss of the strong hydrophobic interactions of gemini surfactants resulting from dissymmetry. The CMC of C₁₀C₁₀Sul is the lowest of all the surfactants studied, possibly because of the large number of carbon atoms in C₁₂C₁₂Sul. It is noteworthy that the CMC values of the longer and shorter hydrophobic groups have an influence on the CMC.

Table 1 The values of CMC, surface tension at the CMC (γ_{CMC}), surface excess concentration (Γ), occupied area per molecule (A), efficiency of adsorption (pC_{20}), effectiveness of adsorption and micellization (CMC/C₂₀), and the standard free energies of micellization and adsorption (ΔG°_mic and ΔG°_ads) for dissymmetric and symmetric anionic gemini surfactants with sulfonic acid groups obtained from the surface tension plots at 25°C.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>n/m</th>
<th>CMC (μmol dm⁻³)</th>
<th>γ_{CMC} (mN m⁻¹)</th>
<th>Γ (mol m⁻²)</th>
<th>A (nm²/molecule)</th>
<th>pC₂₀</th>
<th>CMC / C₂₀</th>
<th>ΔG°_mic (kJ mol⁻¹)</th>
<th>ΔG°_ads (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆C₁₀Sul</td>
<td>1.0</td>
<td>2.21</td>
<td>35.6</td>
<td>3.94</td>
<td>0.42</td>
<td>6.4</td>
<td>9.4</td>
<td>-16.5</td>
<td>-25.7</td>
</tr>
<tr>
<td>C₄C₁₂Sul</td>
<td>1.5</td>
<td>8.33</td>
<td>38.4</td>
<td>2.90</td>
<td>0.57</td>
<td>5.9</td>
<td>7.2</td>
<td>-15.4</td>
<td>-27.0</td>
</tr>
<tr>
<td>C₈C₁₂Sul</td>
<td>1.0</td>
<td>12.5</td>
<td>38.3</td>
<td>1.88</td>
<td>0.88</td>
<td>6.2</td>
<td>18.6</td>
<td>-14.9</td>
<td>-32.7</td>
</tr>
<tr>
<td>C₁₀C₁₀Sul</td>
<td>2.3</td>
<td>9.17</td>
<td>41.0</td>
<td>1.68</td>
<td>0.99</td>
<td>6.2</td>
<td>14.2</td>
<td>-15.2</td>
<td>-33.7</td>
</tr>
<tr>
<td>C₁₂C₁₂Sul</td>
<td>4.0</td>
<td>8.90</td>
<td>44.4</td>
<td>1.34</td>
<td>1.24</td>
<td>6.0</td>
<td>9.8</td>
<td>-15.3</td>
<td>-35.8</td>
</tr>
</tbody>
</table>

The efficiency and effectiveness of surface adsorption can be characterized by the values of the logarithm of the surfactant concentration C₂₀, at which the surface tension of water is reduced by 20 mN m⁻¹, and CMC/C₂₀, respectively. The value of pC₂₀ measures the surfactant-adsorption efficiency at the air/water interface: as the value of pC₂₀ increases, the tendency of the surfactant to adsorb at the air/water interface also increases relative to its tendency to form micelles, and the surfactant becomes more efficient at reducing the surface tension. As shown in Table 1, the pC₂₀ values of all the surfactants studied are almost the same. Generally, the long hydrocarbon chains of conventional surfactants cause strong adsorption at the air/water interface. However, in this study, the adsorption efficiencies of all the surfactants are equal and are not correlated with the CMC, γ_{CMC}, or occupied area per molecule. The value of the CMC/C₂₀ ratio is a convenient way of mea-
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Testing a surfactant’s effectiveness and can be correlated with structural factors involved in the micellization and adsorption processes: as the CMC/C20 ratio increases, the tendency of the surfactant to adsorb at the interface also increases relative to its tendency to form micelles. The effectiveness of the adsorption of C6C12Sul and C8C12Sul exceeds that of C8C12Sul and C10C12Sul. Furthermore, the CMC/C20 ratios of C6C12Sul and C10C12Sul are lower than that of C8C12Sul, indicating that C8C12Sul and C10C12Sul form micelles more readily than C10C12Sul.

The standard free energy of micellization (ΔGmic) for the surfactant ions neutralized by micelle-bound univalent counter ions calculated as

\[ \Delta G_{mic} = RT \ln 2 \]

where \( \beta \) is the fraction of the charges of micellized univalent surfactant ions neutralized by micelle-bound univalent counter ions calculated as \( \beta = 1 - \alpha \). Here, \( \alpha \) is taken to be 1 because the surfactants dissolve completely into surfactant ions and counter ions in NaOH solution. The standard free energy of adsorption (ΔGads) at the air/water interface is calculated by the equation:

\[ \Delta G_{ads} = \Delta G_{mic} - \pi_{cmc} \frac{1}{\Gamma} \]

where \( \pi_{cmc} \) is the surface pressure at the CMC (\( = \gamma_{0} - \gamma_{cmc} \), \( \gamma_{0} \) is the surface tension of water). The values of \( \Delta G_{mic} \) and \( \Delta G_{ads} \) for C6C12Sul are listed in Table 1. The values of \( \Delta G_{mic} \) are larger than those of \( \Delta G_{ads} \) for all the surfactants studied, indicating that adsorption at the air/water interface is favored over micellization. The value of \( \Delta G_{mic} \) for C6C12Sul is the largest of all the surfactants studied, and the value of \( \Delta G_{mic} \) for the dissymmetric surfactants is almost the same. The \( \Delta G_{mic} \) and CMC/C20 results indicate that dissymmetric gemini surfactants undergo micellization more readily than symmetric surfactant. This finding suggests that increasing the number of carbon atoms in the longer chain decreases \( \Delta G_{mic} \). The value of \( \Delta G_{mic} \) for C6C12Sul is the largest of all the dissymmetric surfactants studied. The \( \Delta G_{mic} \) and CMC/C20 results suggest that the micellization of C8C12Sul is more favorable than adsorption at the air/water interface and that this difference is greater for C6C12Sul than for C10C12Sul, C8C12Sul, and C10C12Sul. The values of \( \Delta G_{mic} \) and \( \Delta G_{ads} \) for C6C12Sul indicate that C6C12Sul forms micelles more readily than C10C12Sul but less readily than C10C12Sul. In terms of the surface tension, C6C12Sul exhibits stronger hydrophobic interactions than C8C12Sul but weaker hydrophobic interactions than C10C12Sul. In fact, the hydrophobic interactions of C8C12Sul appear to be only slightly weakened by this surfactant’s small degree of dissymmetry, while they are strengthened by the presence of a dodecyl chain.

3.2 Aggregation properties in solution

The change in the I/I3 ratio as a function of the surfactant concentration for (a) C8C12Sul and C10C12Sul and for (b) C6C12Sul, C10C12Sul, and C12C12Sul is shown in Fig. 3. It is well known that when pyrene is in a hydrophilic environment, the I/I3 ratio becomes nearly 1.8 and decreases as the hydrophobic character of the environment increases. The I/I3 ratios of all the surfactants studied start to decrease at concentration that are 10–20 times higher than the CMC determined based on the surface tension. Thus, at concentrations between the CMC and 10–20 times the CMC, pyrene is not solubilized by surfactants because the only hydrophobic environment consists of surfactant molecules. For the surfactants studied, the I/I3 ratio decreases slowly as the surfactant concentration increase compared with conventional surfactants and reaches a constant value of approximately 1.3 at a concentration of 600–800 times the CMC. This indicates that the hydrophobic character of the environment is maximized at surfactant concentrations exceeding 600–800 times the CMC. The gradual decrease of the I/I3 ratio observed here represents a peculiar case, suggesting that the micelle-formation process of these surfactants differs from that of conventional surfactants.

The change in the hydrodynamic diameter as a function of the surfactant concentration for (a) C8C12Sul, C10C12Sul,
and C_{12}C_{12}Sul and for (b) C_{10}C_{10}Sul and C_{8}C_{12}Sul is shown in Fig. 4. The surfactant concentrations are 5, 50, 200, 400, 600, and 800 times the CMC, except for C_{12}C_{12}Sul, which was also investigated at concentrations of 1000, 1800, and 2000 times the CMC. It should be noted that the scattering intensity at 5 times the CMC was very weak, and the value of the hydrodynamic diameter could not be determined. For all the surfactants studied, the average hydrodynamic diameters decrease as the surfactant concentration increases and remain constant when the surfactant concentration exceeds 600–800 times the CMC. These results confirm the behavior determined using steady-state fluorescence, which showed that the $I_{I/3}$ ratio is constant and the environment surrounding pyrene is the most hydrophobic when the surfactant concentration exceeds 600–800 times the CMC. Therefore, close-packing micelles consisting of surfactant molecules exist in solution when the concentration exceeds 600–800 times the CMC. For the dissymmetric surfactants and C_{10}C_{10}Sul, the hydrodynamic diameters at 800 times the CMC as a function of the carbon number of the longer chain, $n$, are shown in Fig. 5. The hydrodynamic diameters increase as the carbon number of the longer chain, $n$, increases. Thus, the micelle diameter depends on the longer of the two hydrocarbon chains for symmetric and dissymmetric gemini surfactants with the same number of carbon chains. Additionally, the hydrodynamic diameters of dissymmetric gemini surfactants increase as their alkyl chain length increase, and the size of micelles formed by symmetric surfactants also depends on the alkyl chain length.

4 CONCLUSION

In this study, we synthesized dissymmetric anionic gemini surfactants with sulfonic acid groups. We investigated the solution properties of the synthesized surfactants via surface tension, pyrene fluorescence, and DLS measurements. The CMC values of the dissymmetric gemini surfactants were slightly smaller than those of the symmet-
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Dissymmetric gemini surfactants with the same total carbon numbers in their alkyl chains. The surface tension of the symmetric gemini surfactants with two decyl chains reached 38 mN m⁻¹ at the CMC, and increasing the degree of dissymmetry decreased the efficiency in lowering the surface tension. Therefore, gemini surfactants with small degrees of dissymmetry do not lose the strong hydrophobic interactions typical of symmetric gemini surfactants, and as the degree of dissymmetry increases, the hydrophobic interactions of the dissymmetric alkyl chains weaken relative to those of the symmetric surfactant’s chains. Pyrene fluorescence suggested that the micelle-formation process of the studied surfactants differs from that of conventional surfactants. The hydrodynamic diameters of the micelles formed by the dissymmetric gemini surfactants increase as the degree of dissymmetry increases. Therefore, the size of the resulting micelle depends on the longer of the two alkyl chains of dissymmetric gemini surfactants.

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References