Oleic Acid-Based Gemini Surfactants with Carboxylic Acid Headgroups

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Abstract: Anionic gemini surfactants with carboxylic acid headgroups have been synthesized from oleic acid. The hydrocarbon chain is covalently bound to the terminal carbonyl group of oleic acid via an ester bond, and the carboxylic acid headgroups are introduced to the cis double bond of oleic acid via disuccinyl units. The surfactants exhibit pH-dependent protonation–deprotonation behavior in aqueous solutions. In alkaline solutions (pH 9 in the presence of 10 mmol dm⁻³ NaCl as the background electrolyte), the surfactants can lower the surface tension as well as form molecular assemblies, even in the region of low surfactant concentrations. Under acidic (pH 3) or neutral (pH 6–7) conditions, the surfactants are intrinsically insoluble in aqueous media and form a monolayer at the air/water interface. In this study, we have investigated physicochemical properties such as the function of the hydrocarbon chain length by means of static surface tension, pyrene fluorescence, dynamic light scattering, surface pressure–area isotherms, and infrared external reflection measurements.

Key words: gemini surfactant, oleic acid, carboxylic acid headgroup, adsorption, molecular association, monolayer film

1 INTRODUCTION

Gemini surfactants are dimers of monomeric surfactants linked with a spacer at the level of hydrophilic headgroups. The physicochemical aspects of the aqueous solution properties of gemini surfactants have been reviewed in the literature¹⁻⁸. One of the key properties of gemini surfactants is the remarkably low critical micelle concentration (cmc) in aqueous media, which enables us to reduce the total consumption of surfactants in waterborne chemical products. Gemini surfactants are consequently called "environmentally friendly materials." Nevertheless, the number of commercially available gemini surfactants is very limited because the synthesis and subsequent purification process is generally more complicated than that of conventional monomeric surfactants. Their selling price has been a serious problem when providing a wide variety of gemini surfactants to the market.

Based on this background, we have developed oleic acid-based gemini surfactants⁴. Oleic acid is the basis of human sebum and stratum corneum cell lipids, hence it is a bio-compatible and relatively low-cost material. Indeed, based on its chemical structure, we make the following hypotheses. First, it is possible to modify the cis double bond with various kinds of headgroups through relatively simple chemical reactions to achieve cost-effective synthesis. Second, it is possible to introduce a hydrocarbon chain at the terminal carbonyl group via the amide or ester bonding. These two synthetic strategies allow for the design of a wide variety of gemini surfactants as well as for the control of the hydrophilic/hydrophobic balance of the surfactants by variations in the hydrocarbon chain length and the type of headgroups. The oleic acid-based surfactants synthesized in our previous works include phosphate-type⁵ and sulfonic-type⁶ anions.

In our current work, we have developed a new type of oleic acid-based gemini surfactant and studied the physicochemical properties as a function of the hydrocarbon chain length. These surfactants contain two carboxylic acid headgroups covalently bound to the cis double bond of oleic acid via disuccinyl units. The carboxylic acid head-
groups generally exhibit pH-dependent protonation-deprotonation behavior; the physicochemical properties have therefore been characterized both in alkaline solutions and under acidic or neutral conditions (but in the intrinsically insoluble pH region). The aqueous solution properties have been studied on the basis of surface tension, pyrene fluorescence, and dynamic light scattering (DLS) data under acidic (pH 3) or neutral (pH 6-7) conditions. Hereafter, we call the surfactants "CC-9,9-Esn" (see also Fig. 1), where n is the length of the hydrocarbon chain covalently bound to the terminal carbonyl group of oleic acid (n=6, 8, and 10). We note that anionic gemini surfactants with carboxylic acid headgroups have been developed in the past\(^7\)-\(^{12}\); however, physicochemical information on cost-effective anionic gemini surfactants is still required by both academia and industry.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

For the syntheses of the surfactants, we used the following chemicals: oleic acid (PM-810RS, Miyoshi Oil & Fat), oleic acid decyl ester (Wako), formic acid (Wako), boron trifluoride diethyl ether complex (Showa), succinic anhydride (Tokyo Chemical Industry (TCI)), triethylamine (Kokusan), 1-hexanol (TCI), 1-octanol (TCI), and 4-dimethylaminopyridine (TCI). The solvents and salts used for the syntheses and purifications were as follows: ethanol, 2-butanone, acetonitrile, hexane, toluene, potassium carbonate, sodium chloride, sodium sulfate, sodium hydroxide, and hydrochloric acid. We note that the chemicals listed above were of analytical grade and used without further purification. The water used in this study was deionized with a Barnstead NANO Pure Diamond UV system and filtered with a Millipore membrane filter (pore size 0.22 μm).

2.2 Synthesis

The final products, CC-9,9-Esn (n=6, 8, and 10), were synthesized according to the reaction scheme shown in Fig. 1 and characterized with several analytical techniques, including FT-IR (JASCO FT/IR-6100), \(^1\)H-NMR (Bruker AV400M 400 MHz), \(^13\)C-NMR (Bruker AV400M 100 MHz), and ESI-MS (JASCO JMS-T100CS) spectroscopies. Elemental analysis (PerkinElmer 2400 Series II CHNS/O Analyzer) and TG-DTA (Shimadzu DTG-60, ca. 4 mg, 10°C min\(^{-1}\)) measurements were also performed.

2.2.1 9,10-Dihydroxyoctadecanoic acid alkyl esters (n=6, 8, and 10)

Two reaction routes to obtain 9,10-dihydroxyoctadecanoic acid alkyl esters (n=6, 8, and 10) were examined. In the case of the shorter-chain analogues (n=6 and 8), 9,10-dihydroxyoctadecanoic acid was first obtained from oleic acid by chemical reaction with formic acid and hydrogen peroxide\(^{13}\). Then, the mixture of 9,10-dihydroxyoctadecanoic acid (0.28 mol), 1-hexanol (or 1-octanol) (1.45 mol), and BF\(_3\)-Et\(_2\)O (6.3 mmol) was refluxed for 8 h and magnetically stirred using a Dean-Stark apparatus. After this reaction, the reaction mixture was cooled to room temperature with addition of hexane (100 cm\(^3\)). After filtration, the residue was recrystallized from hexane and 2-butanone to give a white crystalline product. The yields were 60% for n=6 and 67% for n=8.

In the case of the longer-chain analogue (n=10), oleic acid decyl ester (0.066 mol) was mixed with formic acid (1.31 mol) in a three-necked reaction flask and hydrogen peroxide (0.069 mol) was added dropwise into the mixture for 30 min. Then, the reaction system was stirred for 24 h at 40°C. After removal of the formic acid phase, the residual organic phase was washed three times with water (26 cm\(^3\)). Then, the organic phase obtained was dissolved in ethanol (59 cm\(^3\)) in the presence of potassium carbonate (0.033 mol), and stirred for 24 h at room temperature. A crude product (with potassium carbonate) was obtained after filtration. This product was dissolved in hexane (65 cm\(^3\)) at 60°C and the solution was washed with hot water (13 cm\(^3\)) three times to remove the potassium carbonate. Finally, the organic phase was recrystallized from hexane.
to give a white crystalline product. The yield of 9,10-dihydroxyoctadecanoic acid decyl ester was 74%. As a typical example, the characterization data of 9,10-dihydroxyoctadecanoic acid decyl ester are shown below.

FT-IR (KBr): 3464 cm⁻¹ (O-H st), 3325 cm⁻¹ (O-H st), and 1730 cm⁻¹ (C=O st).

¹H-NMR (CDCl₃): δ 0.90 (t, 6H, 2CH₃), 1.26-1.63 (m, 42H, 21CH₂), 1.97-2.00 (m, 2H, -CH(OH)-CH(OH)-), 1.98 (t, 2H, CH₂C(=O)-), 3.0 (br, 2H, -CH(OH)-CH(OH)-), and 4.05 ppm (t, 2H, CH₂OC(=O)).

2.3 Measurements

Static surface tension measurements were performed using an Otsuka Electronics ELS-Z2 particle-size analyzer. The obtained scattering data were fitted using an intensity-weighted Marquardt analysis to estimate the diffusion coefficients of the molecular assemblies in aqueous solutions. The hydrodynamic diameter was obtained from the diffusion coefficient using the Stokes-Einstein equation. All

### Table 1: Characterization data of CC-9,9-Esn (n = 6, 8, and 10)

<table>
<thead>
<tr>
<th>n</th>
<th>FT-IR (cm⁻¹)</th>
<th>¹H-NMR (400 MHz, CDCl₃, δ ppm)</th>
<th>¹³C-NMR (100 MHz, CDCl₃, δ ppm)</th>
<th>Molecular formula</th>
<th>HR-MS [M+Na]⁺</th>
<th>Elemental analysis</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3025 (O-H st, 1712, 1731 (C=O st)</td>
<td>0.86-0.91 (m, 6H, 2CH₃), 1.25-1.63 (m, 34H, 17CH₂), 2.29 (t, 2H, CH₂COOCH₃), 2.61-2.73 (m, 8H, 2CH(OOCCOCH₃CH₃COOCH₃)), 4.06 (t, 2H, CH₂COOCH₃), 5.01-5.04 (m, 2H, 2CH(OOCCOCH₃CH₃COOCH₃))</td>
<td>14.0, 14.1 (CH₃), 22.5, 22.6, 25.0, 25.6, 28.6, 28.9, 29.0, 29.1, 29.2, 29.4, 30.8, 31.4, 31.8, 34.3 (CH₃), 64.6 (CH₂COOCH₃), 74.4 (CH(OOCCOCH₃CH₃COOCH₃)), 171.6 (CH(OOCCOCH₃CH₃COOCH₃)), 174.3 (CH₂COOCH₃), 178.2 (CH(OOCCOCH₃CH₃COOCH₃))</td>
<td>C₈H₁₀O₁₁ (calcd.)</td>
<td>623.3776</td>
<td>Found (calcd.)</td>
<td>C₆4.31 (63.97)</td>
</tr>
<tr>
<td>8</td>
<td>3031 (O-H st, 1712, 1731 (C=O st)</td>
<td>0.86-0.90 (m, 6H, 2CH₃), 1.25-1.63 (m, 38H, 19CH₂), 2.29 (t, 2H, CH₂COOCH₃), 2.61-2.70 (m, 8H, 2CH(OOCCOCH₃CH₃COOCH₃)), 4.06 (t, 2H, CH₂COOCH₃), 5.02-5.04 (m, 2H, 2CH(OOCCOCH₃CH₃COOCH₃))</td>
<td>14.1 (CH₃), 22.7, 22.7, 25.0, 25.9, 28.6, 28.9, 29.0, 29.1, 29.2, 29.4, 30.8, 31.8, 34.3 (CH₃), 66.3 (CH₂COOCH₃), 74.4 (CH(OOCCOCH₃CH₃COOCH₃)), 171.6 (CH(OOCCOCH₃CH₃COOCH₃)), 174.3 (CH₂COOCH₃), 178.2 (CH(OOCCOCH₃CH₃COOCH₃))</td>
<td>C₂₀H₂₀O₁₁ (calcd.)</td>
<td>651.4055</td>
<td>Found (calcd.)</td>
<td>C₆6.59 (64.94)</td>
</tr>
<tr>
<td>10</td>
<td>3028 (O-H st, 1712, 1732 (C=O st)</td>
<td>0.86-0.90 (m, 6H, 2CH₃), 1.25-1.63 (m, 42H, 21CH₂), 2.29 (t, 2H, CH₂COOCH₃), 2.61-2.70 (m, 8H, 2CH(OOCCOCH₃CH₃COOCH₃)), 4.05 (t, 2H, CH₂COOCH₃), 5.01-5.04 (m, 2H, 2CH(OOCCOCH₃CH₃COOCH₃))</td>
<td>14.1 (CH₃), 22.7, 24.9, 25.0, 25.9, 28.6, 28.9, 29.0, 29.1, 29.2, 29.4, 29.5, 30.8, 31.8, 31.9, 34.3 (CH₃), 66.3 (CH₂COOCH₃), 74.4 (CH(OOCCOCH₃CH₃COOCH₃)), 171.6 (CH(OOCCOCH₃CH₃COOCH₃)), 174.3 (CH₂COOCH₃), 178.2 (CH(OOCCOCH₃CH₃COOCH₃))</td>
<td>C₂₃H₂₄O₁₁ (calcd.)</td>
<td>679.4372</td>
<td>Found (calcd.)</td>
<td>C₆₈.63 (65.82)</td>
</tr>
</tbody>
</table>
sample solutions were filtered with a 5 μm cellulose acetate membrane filter before the measurements were taken.

π-A isotherm data were obtained using a Kyowa HBM700LB trough with a platinum ring. The surfactant samples were first dissolved in chloroform (1 mmol dm⁻³) and then the solution (70 μL) was spread on either a pH 3 or pH 6-7 aqueous solution.

IER measurements were performed using a Perkin Elmer Spectrum 100 IR spectrometer equipped with an external reflection module. The effective dimensions of the IER liquid cell were 2.25 cm ⨉ 8.3 cm. A surfactant solution dissolved in chloroform (0.1 mmol dm⁻³ for CC-9,9-Es₈) was spread on the water surface and the system was equilibrated for 1 h. The angle of the incident beam was fixed at 30° from the normal at the water surface. The resultant spectroscopic data were always integrated 1200 times in order to improve the signal-to-noise ratio.

Unless otherwise stated, all measurements reported were performed at 25°C (or at a room temperature of ca. 25°C).

3 RESULTS AND DISCUSSION

3.1 Molecular characteristics

As mentioned in Section 2.2, we have confirmed the chemical structure of CC-9,9-Esn on the basis of the analytical data. The two carboxylic acid headgroups are introduced to the cis double bond of oleic acid. This is a remarkable feature of CC-9,9-Esn since oleic acid-based surfactants that we have synthesized in the past exhibit a dissymmetric headgroup structure⁵,⁶. The symmetric headgroups in our current samples exclude the presence of possible regioisomers, although pairs of enantiomers (9R,10R and 9S,10S) must be present in view of the reaction mechanism. We note that one of the carboxylic acid headgroups is in an anti-position with respect to the other carboxylic acid headgroup.

3.2 pH titrations

In order to examine the pH-dependent protonation-deprotonation behavior of CC-9,9-Esn, pH titration measurements were performed for the three analogues. Each surfactant sample was added to pure water without pH adjustment in the absence of added electrolytes, and then an aqueous solution of 10 mmol dm⁻³ NaOH was added dropwise. The surfactant concentration was set at 1 mmol dm⁻³. As a typical example, the pH titration data obtained for n = 8 are shown in Fig. 2. Precipitates are seen in the region of pH 7-8, but the solution transparency gradually increases with increasing pH. We confirmed complete dissolution at pH 8.7. The pH of this solution is very close to the pH at which the two carboxylic acid headgroups are expected to be fully deprotonated by NaOH (pH = 8.9 at [NaOH]/[CC-9,9-Es₈] = 2). Similarly, we confirmed the complete dissolution of CC-9,9-Es₆ at pH 8.4 and of CC-9,9-Es₁₀ at pH 8.8. On the basis of these pH titration data, we have characterized (i) the physicochemical properties of the surfactants dissolved in aqueous media at pH 9, and (ii) the surfactant monolayer formed at the air/water interface either at pH 3 or at pH 6-7, where the surfactant samples are intrinsically insoluble in the media.

3.3 Aqueous solution properties at pH 9

Figure 3 shows the static surface tension of aqueous solutions of CC-9,9-Esn as a function of their concentrations. These measurements were performed at pH 9 in the presence of 10 mmol dm⁻³ NaCl. As mentioned earlier, neither precipitation nor phase separation was seen in the ana-

Fig. 2  pH titration data of a CC-9,9-Es₈ aqueous solution (1 mmol dm⁻³) in the absence of added electrolytes. A NaOH aqueous solution (10 mmol dm⁻³) was added to the surfactant solution and the solution pH was monitored as a function of the molar ratio ([NaOH]/[CC-9,9-Es₈]).

Fig. 3  Static surface tension of aqueous CC-9,9-Esn (n = 6, 8, and 10) solutions as a function of their concentrations. The surfactant solutions contained 10 mmol dm⁻³ NaCl as a background electrolyte, and the solution pH was fixed at 9.
logues under these experimental conditions. In the region of low surfactant concentrations, the surface tension decreases sharply with increasing concentration and attains a break point. The surfactant concentration corresponding to this break point is assumed to be the cac of each surfactant. The surface tension data shown in Fig. 3 allow us to calculate some physicochemical parameters (see Table 2): the surface excess concentration estimated at the cac ($\Gamma_{\text{cac}}$) and the occupied area per molecule adsorbed at the air/aqueous solution interface ($A_{\text{cac}}$) were calculated from the following equations\(^{(18)}\):

\[
\Gamma_{\text{cac}} = -\frac{1}{2.303nRT} \left( \frac{d\gamma}{d\log C} \right) \gamma
\]

\[
A_{\text{cac}} = \frac{1}{N_A \Gamma_{\text{cac}}}
\]

where $\gamma$ is the equilibrium surface tension measured at a surfactant concentration of $C$, $T$ is the absolute temperature, $N_A$ is the Avogadro constant, and $R$ is the gas constant. In this case, the number of adsorption species ($n$ in equation 1) is assumed to be 1 in the presence of 10 mmol dm\(^{-3}\) NaCl\(^{(18)}\). We also calculated $pC_{20}$ for each surfactant to measure the efficiency of adsorption\(^{(20)}\). It is clear from this analysis that an increased chain length results in (i) lower $\Gamma_{\text{cac}}$ (and hence smaller $A_{\text{cac}}$), and (iii) greater $pC_{20}$ values. These findings suggest that the increased chain length yields a closely packed monolayer film at the air/aqueous solution interface at pH 9 because of an increased hydrophobic character. This is consistent with the previous data regarding the aqueous solution properties of oleic acid-based phosphate-type\(^{(5)}\) and sulfonic-type\(^{(8)}\) surfactants, although in this case no significant difference in $\gamma_{\text{cac}}$ is observed as a function of the chain length (in the earlier papers we reported the decreasing $\gamma_{\text{cac}}$ with increasing chain length).

The cac values of CC-9,9-Esn have also been evaluated on the basis of pyrene fluorescence $I_1/I_2$ data. Figure 4 shows the resultant $I_1/I_2$ values as a function of surfactant concentration, obtained at pH 9 in the presence of 10 mmol dm\(^{-3}\) NaCl. For all analogues, the $I_1/I_2$ values start to decrease at a concentration assumed to be each cac. The cac values estimated by these $I_1/I_2$ measurements (0.33 mmol dm\(^{-3}\) for $n = 6$; 0.040 mmol dm\(^{-3}\) for $n = 8$; and 0.0040 mmol dm\(^{-3}\) for $n = 10$) are consistent with the cac values determined by static surface tensiometry (see Table 2).

3.4 Characterization of surfactant monolayer formed under acidic or neutral conditions

Since the surfactants employed in this study exhibit pH-dependent protonation-deprotonation behavior, it is interesting to see interfacial properties in the intrinsically insoluble pH region (see pH titration data, Fig. 2). Figure 6 shows the $\pi$-A isotherm data obtained for the three analogues of CC-9,9-Esn at pH 6-7. The aqueous medium does not contain any additional electrolytes. For the three analogues, the surface pressure increases gradually with de-

**Table 2** Physicochemical properties under the alkaline conditions\(^{(9)}\).

<table>
<thead>
<tr>
<th></th>
<th>cac mmol dm(^{-3})</th>
<th>$\gamma_{\text{cac}}$ mN m(^{-1})</th>
<th>$\Gamma_{\text{cac}}$ mmol m(^{-2})</th>
<th>$A_{\text{cac}}$ nm(^2)</th>
<th>$pC_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-9,9-Es6</td>
<td>0.41</td>
<td>30.1</td>
<td>1.8</td>
<td>0.94</td>
<td>5.2</td>
</tr>
<tr>
<td>CC-9,9-Es8</td>
<td>0.040</td>
<td>30.5</td>
<td>1.9</td>
<td>0.88</td>
<td>6.1</td>
</tr>
<tr>
<td>CC-9,9-Es10</td>
<td>0.0037</td>
<td>30.6</td>
<td>2.6</td>
<td>0.63</td>
<td>6.6</td>
</tr>
</tbody>
</table>

a) Measured in the presence of 10 mmol dm\(^{-3}\) NaCl at pH 9.

![Fig. 4](Image) Pyrene fluorescence $I_1/I_2$ data as a function of CC-9,9-Esn ($n = 6$, 8, and 10) concentration, obtained at pH 9 in the presence of 10 mmol dm\(^{-3}\) NaCl.

It is interesting to characterize the molecular aggregates that spontaneously formed in the alkaline solutions. The hydrodynamic diameters of CC-9,9-Esn, measured at pH 9 in the presence of 10 mmol dm\(^{-3}\) NaCl, are presented in Fig. 5; the surfactant concentration is set at 300×cac for each analogue. Relatively small aggregates are suggested to be formed in the case of the two shorter-chain analogues ($n = 6$ and 8), whereas larger aggregates are observed for the longer-chain analogue ($n = 10$). This may result from a difference in molecular geometry on the basis of the critical packing parameter concept\(^{(20)}\): CC-9,9-Es10 gives a larger packing parameter than CC-9,9-Es6 and CC-9,9-Es8, and hence spontaneously forms less curved molecular aggregates in solutions. It seems likely that the assemblies observed for CC-9,9-Es10 are either aggregates of small micelles or vesicular assemblies.
increases with increasing chain length at a given surface pressure, the degree of homogeneity of the monolayer film increases with increasing chain length. IER measurements provide further insights regarding the chain conformation of the surfactant molecules formed at the air/water interface. These measurements were performed at pH 6-7 in the absence of added electrolytes. Unfortunately, it is not possible to control the molecular area precisely using our IER instrument because the instrument is not equipped with a compression mechanism. Instead, we have studied the effects of molecular packing on the chain conformation by changing the sample volume of the CC-9,9-Es\textsubscript{n} chloroform solution (0.1 mmol dm\textsuperscript{-3}) spread on the water surface. The typical IER spectra of CC-9,9-Es\textsubscript{8} obtained at the interface are given in Fig. 7a. The characteristic absorption peak appears in the range of 2920-2930 cm\textsuperscript{-1}, which originated from the CH\textsubscript{2} asymmetric stretching vibration of the hydrocarbon chains. The wavenumber observed for the absorption peak is plotted in Fig. 7b as a function of the volume of the CC-9,9-Es\textsubscript{8} chloroform solution spread on the water surface.

4 CONCLUSIONS

We have synthesized novel anionic gemini surfactants from oleic acid. The hydrocarbon chain is covalently bound to the terminal carbonyl group of oleic acid and the carboxylic acid headgroups are introduced to the cis double...
bond of oleic acid via disuccinyl units. The surfactants exhibit pH-dependent protonation-deprotonation behavior in aqueous solutions. In alkaline solutions, the surfactants lower the surface tension as well as forming molecular assemblies, even in the region of relatively low concentrations, in a manner similar to oleic acid-based gemini surfactants with phosphate or sulfonic acid headgroups. Under acidic or neutral conditions, the surfactants are intrinsically insoluble in the aqueous media and form a monolayer at the air/water interface. We anticipate that the surfactants developed in this study will find application in the formulation of high-performance chemical products in the field of cosmetics, personal care, medicine, etc.

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References and Notes

19) The C<sub>20</sub> is defined as the surfactant concentration that produces a reduction of 20 mN m<sup>-1</sup> in the surface tension of an aqueous solution of 10 mmol dm<sup>-3</sup> NaCl (pC<sub>20</sub> = − log C<sub>20</sub>), and therefore, this value is indicative of an efficiency in lowering the surface tension. See also reference 18.

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