Sulfonic-Hydroxyl-Type Heterogemini Surfactants Synthesized from Unsaturated Fatty Acids

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Abstract: Novel anionic heterogemini surfactants have been synthesized from two kinds of unsaturated fatty acids (oleic acid and petroselinic acid). The hydrocarbon chain is covalently bound to the terminal carbonyl group of the unsaturated fatty acids and hydrophilic headgroups (i.e., sulfonic and hydroxyl groups) are introduced to the cis double bond. The aqueous solution properties of the surfactants synthesized here have been studied on the basis of static/dynamic surface tension, conductivity, fluorescence, and dynamic light scattering (DLS) data. We have mainly focused on the following two factors that may significantly impact the aqueous solution properties of the surfactants: one is hydrocarbon chain length and the other is molecular symmetry. The first key result from our current study is that increased hydrocarbon chain length results in a closely packed monolayer film at the air/aqueous solution interface, even at low concentrations as a result of the increased hydrophobicity of the longer chain analogue. We have previously observed a similar trend when aqueous solution properties of oleic acid-based phosphate-type heterogemini surfactants were studied. The second key finding of our current research is that increased molecular symmetry results in greater surface activities (which include lower aqueous surface tension and greater molecular packing at the air/aqueous solution interface). In addition, it seems likely that the size of molecular assemblies spontaneously formed in bulk solution decreases when the molecular symmetry increases. These results suggest that the symmetric analogue provides greater hydrophobic environments, although the exact reason for this is not yet known.

Key words: Gemini surfactant, sulfonic headgroup, molecular symmetry, surface tension, molecular association

1 INTRODUCTION

Gemini surfactants, which consist of two monomeric surfactants linked with a spacer, are an important class of functionalized amphiphilic molecules with remarkable physicochemical properties. When compared with conventional monomeric surfactants, the corresponding Gemini surfactants generally present (i) a lower critical micelle concentration (cmc), (ii) a lower surface tension measured at the cmc, (iii) spontaneous formation of vesicles and/or wormlike micelles even at relatively low concentrations, and (iv) a lower Krafft temperature and good water solubility in the case of ionic Gemini surfactants. These physicochemical properties of Gemini surfactants enable us to reduce total consumption of chemicals in industrial products, and therefore, Gemini surfactants are deemed to be environmental green materials. Nevertheless, the number of commercially available Gemini surfactants is very limited, because their synthesis is more complicated than that of monomeric surfactants. As a result, the synthesis and purification costs associated with Gemini surfactants are problematic. In order to use Gemini surfactants in a wide variety of applications, cheaper synthesis and purification strategies are necessary.

In our previous paper,4 we presented aqueous solution properties of anionic (hetero) Gemini surfactants containing a phosphate headgroup that were synthesized from oleic...
acid derivatives. Oleic acid is the basis of human sebum and stratum corneum cell lipids, and hence it is a biocompatible, ecological, and relatively cheap material. Indeed, from the standpoint of its chemical structure, we hypothesize that it is possible to modify the cis double bond with hydrophilic headgroups as well as introduce hydrocarbon chains at the terminal carbonyl group. This enables us to design a wide variety of (hetero)gemini surfactants, and the hydrophilic/hydrophobic balance of the designed surfactants is able to be controlled by changing the hydrocarbon chain length and the type of hydrophilic headgroups. This allows for the development of environmental surfactants for a wide variety of industrial applications. Based on a similar strategy, Alami and co-workers have reported oleylnitrile-based nonionic heterogemini surfactants containing hydroxyl and polyoxyethylene headgroups and oleylnitrile-based anionic heterogemini surfactants containing sulfate and polyoxyethylene headgroups.

Herein, in order to increase the varieties of oleic acid-based heterogemini surfactants, we demonstrate the synthesis and aqueous solution properties of oleic acid-based anionic heterogemini surfactants containing a sulfonic headgroup. The surfactants were synthesized according to the scheme shown in Fig. 1a. This procedure gives heterogemini surfactants containing dissymmetric headgroups (either sulfonic–hydroxyl (SOH) type or sulfonic–sulfate (SS) type) with dissymmetric hydrocarbon chains. Hereafter, we refer to the surfactants as ‘SOH-9,9-Amν’ and

![Fig. 1](image-url)

**Fig. 1** (a) Synthetic route of SOH-9,9-Amν and SS-9,9-Amν (n = 8, 10, and 12) from oleic acid; (b) Possible regioisomers and enantiomers of SOH-9,9-Amν; (c) Chemical structure of (9R-SO₃Na, 10R-OH) SOH-9,9-Am₁₀, as a typical example, represented by the Newman projection; (d) Chemical structure of SOH-12,6-Am₁₀ synthesized from petroselinic acid.
SS-9,9-Amn\textsuperscript{n}, respectively, where \( n \) is the hydrocarbon chain length covalently bound to the terminal carbonyl group in oleic acid (\( n = 8, 10, \) and 12). This paper only focuses on the surfactant series of SOH-9,9-Am\textsuperscript{n} (as a function of \( n \), Section 3.2), and the series of SS-9,9-Am\textsuperscript{n} will be discussed in a future publication.

Wang and co-workers have reported that molecular symmetry significantly impacts the aqueous solution properties of heterogemini surfactants\textsuperscript{7}. In our current case, changing the hydrocarbon chain length also results in a change in the molecular symmetry. In order to understand the effects of the molecular symmetry of SOH-9,9-Am\textsuperscript{n} on aqueous solution properties, we also synthesized petroselinic acid-based heterogemini surfactants and studied their aqueous solution properties. The hydrocarbon chain length of this unsaturated fatty acid is the same as oleic acid, but the cis double bond lies at the 6-7 position, which is different from oleic acid (9-10 position). As a result, petroselinic acid yields heterogemini surfactants whose molecular symmetry is different from SOH-9,9-Am\textsuperscript{n} (under a fixed hydrocarbon chain length). We named the petroselinic acid-based heterogemini surfactants 'SOH-12,6-Amn\textsuperscript{n}' (and 'SS-12,6-Amn\textsuperscript{n}') in Section 3.3. We present the aqueous solution properties of SOH-12,6-Am10 and compare the physicochemical data with the corresponding data for SOH-9,9-Am10.

2 EXPERIMENTAL

2.1 Materials

For the syntheses of the surfactants, we used the following chemicals: high purity oleic acid (SOF), petroselinic acid (Wako Pure Chemical Industries), sulfur trioxide (Wako), anhydrous 1,4-dioxane (Wako), 1-aminoctane (Tokyo Chemical Industry, TCI), 1-amidoheptane (TCI), 1-aminoctadecane (TCI), oxalyl chloride (TCI), and anhydrous pyridine (Wako). The solvents and salts used for the syntheses and purifications included dichloromethane, dichloroethane, chloroform, methanol, ethanol, 1-butanol, acetone, ethyl acetate, acetonitrile, tetrahydrofuran, hexane, diethylether, 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 (0.22 \( \mu \)m in pore size).

2.2 Synthesis

The final products, SOH-9,9-Am\textsuperscript{n} (\( n = 8, 10, \) and 12) and SOH-12,6-Am10, were synthesized according to the reaction scheme shown in Fig. 1a and characterized by FT-IR (JASCO FT/IR-6100), \(^1\)H-NMR (JEOL-EC/ 125 MHz), and ESI-MS (FT-ICR MS Varian 910-MS) spectroscopies.

2.2.1 SOH-9,9-Am\textsuperscript{n} (\( n = 8, 10, \) and 12)

\( N\)-alkylglycylamide was obtained according to the procedure mentioned in our previous paper\textsuperscript{4}. Anhydrous dichloroethane (30 cm\textsuperscript{3}) was added to gently heated liquid SO\textsubscript{3} (25 mmol, 2 g) under an argon atmosphere in a three-necked reaction flask. The reaction system was ice-cooled below \(-5 \, ^\circ\)C and then anhydrous 1, 4-dioxane (25 mmol, 2.18 g) was added dropwise to the reaction mixture. After this addition, the reaction mixture was stirred for 2 h at temperatures below \(-5 \, ^\circ\)C. \( N\)-alkylglycylamide (e.g., 12.5 mmol (5.23 g) in the case of \( n = 10 \)) dissolved in dichloroethane (50 cm\textsuperscript{3}) was added dropwise to the SO\textsubscript{3}-dioxane dichloroethane solution. The reaction mixture was further stirred for 40 h at room temperature. After the addition of water (10 cm\textsuperscript{3}), the mixture was stirred for 2 h. The reaction solvent was evaporated under reduced pressure in the presence of ethanol. The residue obtained was dissolved in a mixture of water and 1-butanol and then the pH of the solution was adjusted to 6.5 using a sodium hydroxide solution. After extraction, the 1-butanol phase was dehydrated in the presence of sodium sulfate. After removing the sodium sulfate (by filtration), the filtrate was evaporated under reduced pressure. A light yellow crystalline crude product was obtained and purified by column chromatography (Wako C-200 silica gel, chloroform/methanol = 10/1 in volume). A white plate-like crystalline product was obtained (e.g., 3.2 mmol (1.74 g), 27 % yield, for \( n = 10 \)). Further purification was performed via recrystallization from a mixture of dichloromethane and acetonitrile.

2.2.2 SOH-12,6-Am10

The chemical modification of petroselinic acid by 1-aminoheptane was conducted in a similar procedure to the synthesis of \( N\)-alkylglycylamide from oleic acid\textsuperscript{9}. The product synthesized from petroselinic acid (\( N\)-decylcococtadec-12-enamide) was then reacted with SO\textsubscript{3}-dioxane in dichloroethane following the procedure mentioned in Section 2.2.1 (SOH-9,9-Am\textsuperscript{n}).

2.3 Measurements

The aqueous surfactant solutions were prepared via direct dissolution of the white crystalline samples. All measurements reported herein were performed at 25 \( ^\circ\)C.

The static surface tension was measured using a Kyowa Wilhelmy auto surface tensiometer CBVP-Z with a platinum plate. Note that the measurements were continuously carried out until a change in the surface tension became less than 0.1 mN m\textsuperscript{-1} per 120 min. The equilibrium surface tension values were obtained within 2-3 h at higher surfactant concentrations, whereas a longer equilibration time (ca. 7-10 h) was required for lower concentrations.

The dynamic surface tension (\( \gamma_t \)) was estimated using a Krüss BP2 MK2 bubble pressure tensiometer, applying the
following equation:
\[ \gamma = \frac{r}{2} \left( P_{\text{max}} - P_c \right) \]  
where \( P_{\text{max}} \) is the maximum bubble pressure at the air/aqueous solution interface, \( P_c \) is the pressure measured in a capillary for the air/pure water interface, and \( r \) is the inner radius of the capillary. The measurements were conducted with effective surface ages of 5 ms to 50 s.

Conductivity measurements were performed using a TOA CM-40S conductivity meter with a CGT-511B electrode.

In order to estimate the micro-environmental polarity of the micelle interiors, steady-state fluorescence measurements were performed for surfactant solutions containing pyrene as a fluorescence probe, using a Shimadzu RF-5300PC fluorescence spectrophotometer. The spectrum was recorded between 360 and 390 nm with the excitation wavelength of 330 nm. The concentration of pyrene was recorded between 360 and 390 nm with the excitation wavelength of 330 nm. The concentration of pyrene was estimated by the fluorescence intensity ratio of the first (373 nm) to the third (384 nm) vibrational peaks \( \left( \frac{I_1}{I_3} \right) \) indicates the micro-environmental polarity around the pyrene molecules. A decrease in the \( \frac{I_1}{I_3} \) value is indicative of the formation of more hydrophobic environments. The critical association concentration \( \left(\text{cac}\right) \) of each surfactant is determined as the concentration where the \( \frac{I_1}{I_3} \) value starts to decrease.

The hydrodynamic diameter of molecular assemblies in aqueous surfactant solutions was estimated using an IBC NICOMP 380ZLS particle size analyzer equipped with a 5 mW He–Ne laser at a constant detector angle of 90°. The obtained scattering data were fitted using an intensity-weighted cumulative analysis to estimate the diffusion coefficient of the molecular assemblies in aqueous solution. The hydrodynamic diameter was obtained from the diffusion coefficient using the Stokes–Einstein equation. All sample solutions were filtered with a 5 μm cellulose acetate membrane filter before measurements were taken.

### 3 RESULTS AND DISCUSSION

#### 3.1 Molecular characteristics

The characterization data are summarized in **Table 1**. For the surfactant series of SOH-9,9-Am\(n\), the \( ^{13} \text{C}-\text{NMR} \) data show splitting of two characteristic signals: one is assigned to \( \text{CH} (\text{SO}_3\text{Na}) \) (e.g., \( \delta = 65.97 \) and 65.99 ppm in the case of \( n = 10 \)) and the other is assigned to \( \text{CH} (\text{OH}) \) (e.g., \( \delta = 72.36 \) and 72.41 ppm in the case of \( n = 10 \)). These data suggest that SOH-9,9-Am\(n\) is a mixture of its regioisomers, where the sulfonic group is covalently bound to the cis double bond either at the 9 or 10 position (Fig. 1b). Indeed, the reaction mechanism suggests that the sulfonic group must be in an anti position with respect to the hydroxyl group. On the basis of these experimental results and considerations, we assume that each SOH-9,9-Am\(n\) sample synthesized in our current study contains the two regioisomers and their enantiomers (9R, 10R and 9S, 10S) in equivalent molar ratios. A similar situation was reported in our previous paper regarding phosphate-type heterogemini surfactants synthesized from oleic acid.

In the case of SOH-12,6-Am10, its \( ^{13} \text{C}-\text{NMR} \) spectrum does not show splitting of the two corresponding signals: \( \delta = 66.01 \) ppm assigned to \( \text{CH} (\text{SO}_3\text{Na}) \) and \( \delta = 72.37 \) ppm assigned to \( \text{CH} (\text{OH}) \). This indicates that the SOH-12,6-Am10 sample is selectively synthesized without regioisomers, although its enantiomers must be present when the reaction mechanism is taken into consideration (6R, 7R and 6S, 7S). Such a difference in the stereochemistry may result from the combination of the following two factors: one is the intramolecular distance between the amide group and the cis double bond and the other is the molecular symmetry. It seems likely, however, that the former factor is predominant over the latter one since the steric environment around the cis double bond is assumed to be more or less similar for the two compounds.

#### Table 1 Molecular Characterization of SOH-9,9-Am\(n\) \((n = 8, 10, \) and 12) and SOH-12,6-Am10

<table>
<thead>
<tr>
<th>Name</th>
<th>FT-IR (cm(^{-1}))</th>
<th>(^{1} \text{H}-\text{NMR} ) (500 MHz, CD,OD, ppm)</th>
<th>(^{13} \text{C}-\text{NMR} ) (125 MHz, CD,OD, ppm)</th>
<th>Molecular formula</th>
<th>HR-MS [M+Na]</th>
<th>Elemental analysis</th>
</tr>
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<tbody>
<tr>
<td>SOH-9,9-Am8</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Found (calc.)</td>
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<tr>
<td>2854 (C-H α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td>14.4 (CHa), 23.7-33.3 (CHa), 37.1 (CHa-CH2-O), 72.27-72.32 (CH2-OH), 176.1 (CO3-Na)-NH</td>
<td>C16H10NO5SNa</td>
<td>490.3566</td>
<td>C16H10NO5SNa</td>
<td></td>
</tr>
<tr>
<td>1644 (C-O α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td></td>
<td></td>
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<td></td>
<td>Found (calc.)</td>
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<tr>
<td>1173 (S-O α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found (calc.)</td>
</tr>
<tr>
<td>SOH-9,9-Am10</td>
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<td>Found (calc.)</td>
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<tr>
<td>2854 (C-H α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td>14.5 (CHb), 23.7-33.4 (CHb), 37.1 (CHb-CH2-O), 72.27-72.32 (CH2-OH), 176.1 (CO3-Na)-NH</td>
<td>C16H10NO5SNa</td>
<td>490.3566</td>
<td>C16H10NO5SNa</td>
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<tr>
<td>1644 (C-O α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td></td>
<td></td>
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<td></td>
<td>Found (calc.)</td>
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<tr>
<td>1173 (S-O α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td></td>
<td></td>
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<tr>
<td>SOH-9,9-Am12</td>
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<td>14.4 (CHb), 23.7-33.4 (CHb), 37.1 (CHb-CH2-O), 72.27-72.32 (CH2-OH), 176.1 (CO3-Na)-NH</td>
<td>C16H10NO5SNa</td>
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<td>C16H10NO5SNa</td>
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<td>Found (calc.)</td>
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<td>SOH-12,6-Am10</td>
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<td></td>
<td></td>
<td></td>
<td>Found (calc.)</td>
</tr>
<tr>
<td>2852 (C-H α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td>14.4 (CHb), 23.7-33.4 (CHb), 37.1 (CHb-CH2-O), 72.27-72.32 (CH2-OH), 176.1 (CO3-Na)-NH</td>
<td>C16H10NO5SNa</td>
<td>490.3566</td>
<td>C16H10NO5SNa</td>
<td></td>
</tr>
<tr>
<td>1644 (C-O α)</td>
<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
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<td></td>
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<td>Found (calc.)</td>
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<tr>
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<td>3.13-3.16 (br, 2H, NH-CH2), 3.96-3.97 (br, 2H, CH-CH(OH))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found (calc.)</td>
</tr>
</tbody>
</table>
Sulfonic-Hydroxyl-Type Heterogemini Surfactants

3.2 Effects of hydrocarbon chain length on physicochemical properties of aqueous SOH-9,9-Amn solutions (n = 8, 10, and 12)

As mentioned in the Introduction section, we have characterized two factors that significantly impact the aqueous solution properties of SOH-type heterogemini surfactants: one is the hydrocarbon chain length (n) and the other is the degree of molecular symmetry of the surfactants. In this section, we focus on hydrocarbon chain length by studying three surfactant systems (i.e., SOH-9,9-Amn, n = 8, 10, and 12). In our previous work, we studied the aqueous solution properties of phosphate-type heterogemini surfactants synthesized form oleic acid, so the main interest we focus here is if we can see any different trends in the aqueous solution properties between the two surfactant systems.

Figure 2 shows the static surface tension of aqueous solutions of SOH-9,9-Amn (n = 8 and 10) as a function of their concentrations. For the two analogues, in the region of low surfactant concentration, the surface tension decreases sharply with increasing concentration, and finally 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. 2 allow us to calculate some physicochemical parameters (see Table 2), including the surface excess concentration estimated at the air/aqueous solution interface \( \Gamma_{\text{cac}} \), and the occupied area per molecule adsorbed at the air/aqueous solution interface \( A_{\text{cac}} \), using the following equations:

\[
\Gamma_{\text{cac}} = -\frac{1}{2.303 nRT} \left( \frac{d\gamma}{d\log C} \right)_{\gamma_{\text{cac}}} \tag{2}
\]

\[
A_{\text{cac}} = \frac{1}{N_A \Gamma_{\text{cac}}} \tag{3}
\]

where \( \gamma \) is the equilibrium surface tension measured at the surfactant concentration of \( C \), \( T \) is the absolute temperature, \( N_A \) is Avogadro’s number, and \( R \) is the gas constant. In our current case, the number of adsorption species (\( n \) in equation 2) is assumed to be 2. We also calculated the pC\(_{20}\) values for each surfactant to measure the efficiency of adsorption. Here, \( C_{20} \) is defined as the surfactant concentration that produces a reduction of 20 mN m\(^{-1}\) in the surface tension of pure water \( (pC_{20} = -\log C_{20}) \), and therefore, this value is indicative of efficiency in lowering the surface tension. It is clear from this analysis that the longer chain analogue (SOH-9,9-Am10) gives (i) lower \( \gamma_{\text{cac}}, \) (ii) lower \( \gamma_{\text{cac}}, \) (iii) greater \( \Gamma_{\text{cac}} \) (and hence smaller \( A_{\text{cac}} \)), and (iv) greater \( pC_{20} \) values. These results suggest that the longer chain analogue forms a closely packed monolayer film at the air/aqueous solution interface even at lower concentrations as a result of its greater hydrophobic character when compared with the shorter chain analogue (SOH-9,9-Am8).

Also listed in Table 2 are the physicochemical data of phosphate-type POH-9,9-Amn (n = 8 and 10) aqueous solutions, which were presented in our previous paper. Although the experimental conditions are different from our current conditions (i.e., the aqueous solution properties of POH-9,9-Amn were examined in the presence of 0.1 mol dm\(^{-3}\) NaCl as a background electrolyte), the observed trends are consistent with each other. This indicates that SOH-9,9-Amn behaves in a similar manner to POH-9,9-Amn. One can also see in Table 2 that, for a given hydrocarbon chain length, POH-9,9-Amn\( n \) exhibits a greater surface active nature (i.e., lower \( \gamma_{\text{cac}}, \) lower \( \gamma_{\text{cac}}, \) greater \( \Gamma_{\text{cac}} \) (and hence smaller \( A_{\text{cac}} \)) and greater \( pC_{20} \)) as compared with SOH-9,9-Amn. Again it should be noted that the POH-9,9-Amn systems were studied in the presence of 0.1 mol dm\(^{-3}\) NaCl. We assume, therefore, that the observed difference in the surface activity primarily results from the ionic strength in the aqueous solutions: the increased electrolyte

![Fig. 2 Static surface tension of aqueous SOH-9,9-Amn (n = 8 and 10) and SOH-12,6-Am10 solutions as a function of their concentration.](image)

Table 2 Physicochemical Properties on the Basis of Surface Tension Data

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>cac (mmol dm(^{-3}))</th>
<th>( \gamma_{\text{cac}} ) (mN m(^{-1}))</th>
<th>( \Gamma_{\text{cac}} ) (( \mu )mol m(^{-2}))</th>
<th>( A_{\text{cac}} ) (nm(^2))</th>
<th>pC(_{20})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOH-9,9-Am8</td>
<td>0.24</td>
<td>33.6</td>
<td>1.0</td>
<td>1.72</td>
<td>5.4</td>
</tr>
<tr>
<td>SOH-9,9-Am10</td>
<td>0.025</td>
<td>32.2</td>
<td>1.2</td>
<td>1.33</td>
<td>6.0</td>
</tr>
<tr>
<td>SOH-12,6-Am10</td>
<td>0.0068</td>
<td>27.1</td>
<td>1.4</td>
<td>1.21</td>
<td>6.8</td>
</tr>
<tr>
<td>POH-9,9-Am8</td>
<td>0.044</td>
<td>29.5</td>
<td>2.3</td>
<td>0.72</td>
<td>6.1</td>
</tr>
<tr>
<td>POH-9,9-Am10</td>
<td>0.011</td>
<td>29.3</td>
<td>2.6</td>
<td>0.65</td>
<td>6.5</td>
</tr>
</tbody>
</table>

\(^{a}\)From reference 4, measured in the presence of 0.1 mol dm\(^{-3}\) NaCl at pH 7.
concentration causes a significant reduction of the intermolecular electrostatic repulsion and hence greater surface activity is seen in the POH-9,9-Am\(n\) systems.

The cac values of SOH-9,9-Am\(n\) (\(n = 8\) and 10) have also been evaluated on the basis of analytical data obtained from pyrene fluorescence \(I/\bar{I}\) and conductivity measurements. The evaluated cac data are summarized in Table 3. For both analogues, the cac values estimated by the three measurement techniques are consistent with each other, although an accurate cac value of SOH-9,9-Am8 was not determined by the conductivity measurements because of the absence of a definite inflection point.

Finally, we note that SOH-9,9-Am12 precipitates over a wide range of concentrations investigated due to its low water solubility. This means that the Krafft temperature of SOH-9,9-Am12 is above the measured temperature of 25°C.

### 3.3 Effects of molecular symmetry on the physicochemical properties of aqueous SOH-9,9-Am10 and SOH-12,6-Am10 solutions

It has been reported that molecular symmetry of heterogemini surfactants plays a significant role in their aqueous solution properties\(^5\). In our current work, we have studied this effect using two heterogemini surfactants, SOH-9,9-Am10 and SOH-12,6-Am10. The total number of methylene units is identical for the two surfactants (\(\alpha + \beta = 28\), where \(\alpha\) and \(\beta\) are the heterogemini chain lengths), but the degree of molecular symmetry differs (i.e., \(\alpha/\beta = 9/19 = 2.1\) for SOH-9,9-Am10 and \(\alpha/\beta = 16/12 = 1.3\) for SOH-12,6-Am10, respectively). The key experimental findings are discussed below.

The static surface tension data of the two surfactants are shown in Fig. 2 as a function of their concentrations. The physicochemical properties calculated on the basis of the static surface tension data are summarized in Table 2. Clearly, the increased molecular symmetry results in (i) lower cac, (ii) lower \(\gamma_{\text{mic}}\), (iii) greater \(R_{\text{mic}}\) (and hence smaller \(A_{\text{mic}}\)), and (iv) greater \(pC_{\text{20}}\) values. These results suggest that SOH-12,6-Am10 exhibits greater surface activity as compared with SOH-9,9-Am10. From these data, we assume that the more symmetric analogue (SOH-12,6-Am10) provides greater hydrophobic environments within the molecule.

The adsorption kinetics for the air/aqueous solution interface are also different between the two surfactants. SOH-9,9-Am10 adsorbs faster than SOH-12,6-Am10, as shown in Fig. 3. We note that the concentration (0.5 mmol dm\(^{-3}\)) used to measure the dynamic surface tension is well above the cac for each surfactant. Here we see that if the molecular hydrophobicity is a predominant factor in determining the adsorption kinetics, the more hydrophobic SOH-12,6-Am10 must lower the surface tension faster than the less hydrophobic SOH-9,9-Am10. However, this is not consistent with the experimental results. In addition, a difference in the overall molecular size is negligibly small between the two surfactants. This means that, in our current case, the population of molecularly dissolved monomers in solution (apparently, this corresponds to the cac of each surfactant) plays a predominant role in their adsorption kinetics\(^5\) over the other factors such as the molecular hydrophobicity or the overall size of surfactant molecules. The difference in the molecular symmetry, therefore, affects the adsorption kinetics through its effect on the cac of the surfactants.

The lower cac of SOH-12,6-Am10 (than SOH-9,9-Am10) is also supported by pyrene fluorescence \(I/\bar{I}\) and conductivity measurements (see Table 3). Here we would like to present the specific conductivity data versus concentration, in order to estimate the apparent degree of dissociation of counterions from assembly surfaces, by calculating the slope ratio below and above the inflection point (Fig.

### Table 3 CAC Values Evaluated by Some Analytical Techniques (mmol dm\(^{-3}\))

<table>
<thead>
<tr>
<th></th>
<th>Surface tension</th>
<th>Fluorescence (I/\bar{I})</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOH-9,9-Am8</td>
<td>0.24</td>
<td>0.30</td>
<td>–</td>
</tr>
<tr>
<td>SOH-9,9-Am10</td>
<td>0.025</td>
<td>0.025</td>
<td>0.024</td>
</tr>
<tr>
<td>SOH-12,6-Am10</td>
<td>0.0068</td>
<td>0.012</td>
<td>0.0058</td>
</tr>
</tbody>
</table>

Fig. 3 Dynamic surface tension of aqueous SOH-9,9-Am10 and SOH-12,6-Am10 solutions as a function of surface age. The surfactants concentration is fixed at 0.5 mmol dm\(^{-3}\) (> cac of each surfactant).
Sulfonic-Hydroxyl-Type Heterogemini Surfactants


The value is estimated to be 0.49 for SOH-9,9-Am10 and 0.69 for SOH-12,6-Am10. These data indicate that increased molecular symmetry results in increased dissociation of counterions from assembly surfaces, which may occur when SOH-12,6-Am10 assemblies (or their aggregation number) are smaller than SOH-9,9-Am10 assemblies. Our DLS measurements support this possibility. The less symmetric SOH-9,9-Am10 sample gives assemblies whose main hydrodynamic diameter in volume analysis is ca. 200 nm, as shown in Fig. 5. Based on our previous results (oleic acid-based POH-type heterogemini surfactants)⁴, the observed assemblies are assumed to be vesicular aggregates. In contrast, it was hard to obtain reproducible and accurate DLS data in the case of the more symmetric SOH-12,6-Am10 sample, because of its low/unstable scattering intensities during the measurement (at least at 10 mmol dm⁻³), resulting presumably from the formation of smaller assemblies when compared with SOH-9,9-Am10.

In summary, the more symmetric SOH-12,6-Am10 sample exhibits greater surface activities in lowering the aqueous surface tension and in molecular packing at the air/aqueous solution interface. This is attributed to the greater hydrophobic character of SOH-12,6-Am10, and hence we see the decreased cac. The greater hydrophobicity of SOH-12,6-Am10 also results in the closer packing of molecular assemblies whose diameter is suggested to be relatively smaller than that of SOH-9,9-Am10 assemblies. This is not rationalized by the consideration of surfactant geometry on the basis of packing parameter¹³, since rough calculations do not suggest remarkable differences in the overall packing parameter between the two surfactants.

We note that Wang and co-workers have reported opposite behaviors⁷. They have studied aqueous solution properties of cationic heterogemini surfactants (α-6-β, where α and β represent the hydrocarbon chain lengths under the fixed total carbon number of α + β = 24) as a function of their dissymmetry (i.e., α/β) and found the decreased cmc with decreasing symmetry. For this reason, the authors have suggested the possibility that an intermolecular hydrophobic attraction caused by the dissymmetric hydrocarbon chains plays an important role in micellization. It is challenging to resolve the opposite trends observed in our current study and the Wang’s study, since the chemical structures are totally different from each other (e.g., headgroup structure and spacer length). Despite the difficulty of this analysis, we believe that the observed difference in the hydrophobicity between SOH-9,9-Am10 and SOH-12,6-Am10 results from the stereochemistry of the hydrophobic chains linked by a very short spacer (see Fig. 1c). This may provide hydrophobic environments between the two chains (not only within a molecule but also between neighboring molecules); and if this is true, it seems likely that the degree of molecular hydrophobicity is increased with increasing molecular symmetry. In addition, the anti position of the sulfonic group against the hydroxyl group enables the SOH-type surfactants to form a closely packed adsorbed layer at the air/aqueous solution interface as a result of their ‘eclipsed’ conformation, where the two hydrophilic headgroups spread parallel with the air surface and the two hydrophobic chains are normally oriented to the interface, resulting in the formation of the greatest intramolecular hydrophobic environments¹⁴.

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Fig. 4 Specific conductivity of aqueous SOH-9,9-Am10 and SOH-12,6-Am10 solutions as a function of their concentration.

Fig. 5 Apparent hydrodynamic diameter of molecular assemblies of SOH-9,9-Am10 (at 10 mmol dm⁻³).
4 CONCLUSIONS

We have synthesized novel anionic heterogemini surfactants from unsaturated fatty acids (oleic acid and petroselinic acid). The hydrocarbon chain is covalently bound to the terminal carbonyl group of the unsaturated fatty acids and the hydrophilic headgroups (i.e., sulfonic and hydroxyl groups in the current example) are introduced at the cis double bond. The aqueous solution properties have been studied in detail as functions of hydrocarbon chain length and molecular symmetry. The combination of physicochemical data for aqueous SOH-9,9-Am8 and SOH-9,9-Am10 solutions suggests that the longer chain analogue forms a closely packed monolayer film at the air/aqueous solution interface even at lower concentrations as a result of its increased hydrophobic character when compared with the shorter analogue. This result was also observed in a previous system we studied (phosphate-type heterogemini surfactants synthesized from oleic acid) and no remarkably different trends in the aqueous solution properties are seen between the two systems. The use of SOH-9,9-Am10 and SOH-12,6-Am10 leads to the conclusion that the more symmetric SOH-12,6-Am10 sample exhibits greater surface activities in lowering the aqueous surface tension and in molecular packing at the air/aqueous solution interface. The exact reason for this is not yet understood, but we assume that the stereochemistry of hydrophobic chains is a key factor in determining the molecular hydrophobicity.

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References