Polymerizable Anionic Gemini Surfactants: Physicochemical Properties in Aqueous Solution and Polymerization Behavior

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Abstract: A novel polymerizable anionic gemini surfactant has been synthesized and the physicochemical properties in aqueous solution have been studied with a combination of various analytical techniques. The surfactant (PA12-2-12) contains two anionic monomeric parts linked with an ethylene spacer and polymerizable methacryloxy groups covalently bound to the terminal of the hydrocarbon chains. The static surface tension data suggest that, when compared with a conventional (non-polymerizable) anionic gemini surfactant (A12-2-12), (i) the interfacial adsorption of PA12-2-12 occurs more effectively from low surfactant concentrations, whereas (ii) a weak interaction of the polymerizable terminal groups with water molecules (and/or the steric hindrance of the polymerizable groups) plays a significant role in the subsequent molecular packing at the air/aqueous solution interface. The latter effect (as well as the electrostatic repulsion between the anionic headgroups) results in a relatively less packed monolayer film, overcoming the strong intermolecular attractive interaction that is frequently seen for gemini surfactant systems. In the region of low added electrolyte concentrations, PA12-2-12 spontaneously forms spherical micelles in aqueous solution, which is confirmed with the Corrin-Harkins analysis (critical micelle concentration (cmc) vs. total counter-ion concentration) and cryogenic transmission electron microscopy (cryo-TEM). The spherical micelles have been polymerized under UV light irradiation in the absence of added electrolytes. Cryo-TEM measurements confirm that no significant change in the original micelle morphology occurs during the polymerization. This offers a possibility that the polymerizable anionic gemini surfactant should be useful as nano-structural organic templates and/or interfacial stabilizers in aqueous solution.

Key words: gemini surfactant, polymerization, physicochemical property, micelle

1 INTRODUCTION

Gemini surfactants, consisting of two monomeric surfactants linked with a spacer, have been synthesized with a view to developing 'next-generation' high-quality surfactants. When compared with a conventional monomeric surfactant, the corresponding gemini surfactants generally present e.g. (i) a significantly lower critical micelle concentration (cmc), (ii) a lower surface tension measured at the cmc and (iii) greater ability in increasing viscosity of dilute aqueous solutions. Indeed, a structural transformation from spherical micelles to vesicles and/or elongated worm-like micelles is observed even in a dilute aqueous solution of gemini surfactants, being reflective of their larger packing parameter than that of the corresponding monomeric surfactants. Although the synthetic process of gemini surfactants is generally more complicated than that of monomeric ones (and thereby, the synthetic costs are still problematic), these physicochemical properties of gemini surfactants are highly promising for applications in various fields.
surfactants may reduce total consumption of substances in chemical products. Therefore, gemini surfactants themselves are deemed to be an environmental material.

Gemini surfactants modified with polymerizable groups were first reported by Pindzola and co-workers in 2003\(^6\). Such polymerizable surfactants (sometimes called “surfmers”) have been developed for enhancing kinetic and/or mechanical stability of molecular assemblies in aqueous solution\(^6\). This means that polymerized structures are insensitive to dilution effects and that polymerized assemblies persist even below the cmc of the original non-polymerized micelles\(^5\). There is a good review focusing on polymerizable surfactants, in which one can see a lot of polymerized micelles\(^7\). There is a good review focusing on polymerizable surfactants, in which one can see a lot of polymerized micelles\(^7\). There is a good review focusing on polymerizable surfactants, in which one can see a lot of polymerized micelles\(^7\). There is a good review focusing on polymerizable surfactants, in which one can see a lot of polymerized micelles\(^7\). There is a good review focusing on polymerizable surfactants, in which one can see a lot of polymerized micelles\(^7\).

Recently we developed a novel cationic gemini surfactant with polymerizable terminal groups, 1,2-bis(dimethyl(11-methacryloyloxy)undecylammonio) ethane dibromide\(^5,10\). This surfactant contains two cationic monomeric parts linked with an ethylene spacer at the level of the quaternary ammonium groups, and polymerizable methacryloxy groups covalently bound to the terminal of the hydrocarbon chains. As is generally seen in many gemini surfactant systems, the cmc of the synthesized gemini surfactant (0.5 mmol dm\(^{-3}\) in the absence of added electrolytes) is significantly lower than that of the corresponding polymerizable monomeric surfactant (18 mmol dm\(^{-3}\)). The aqueous surface tension measured at the cmc (\(\gamma_{\text{cmc}}\)) also depends on the surfactant type: the gemini surfactant is able to lower aqueous surface tension more effectively than the corresponding monomeric one. We also reported in our previous papers that polymerization of the synthesized gemini surfactant gives (i) spherical micellar aggregates in the absence of added electrolytes without any significant change in the original micelle shape\(^5\) and (ii) tubular hollow assemblies in the region of high electrolyte concentrations (>20 mmol dm\(^{-3}\) NaBr) as a result of structural transformation from vesicular assemblies spontaneously formed in the solution\(^10\). This suggests that it is possible to prepare different shapes of polymerized assemblies by changing the electrolyte concentration, and that such polymerizable gemini surfactants may be useful in developing nano-structural organic templates in aqueous solution, based on a similar concept regarding micelle-structure templating agents\(^5\) and polymerizable emulsion stabilizers\(^5\).

We expect that polymerization occurs more effectively for gemini surfactants than for monomeric ones, resulting from the condensation effect\(^4\) in the gemini structure. In the current work, a novel anionic gemini surfactant modified with polymerizable methacryloxy groups has been developed and aqueous solution properties of the surfactant have been studied. As far as we are aware, such polymerizable anionic gemini surfactants are quite rare\(^15\) and the physiochemical properties based on colloid and interface chemistry have not been studied in detail yet. Indeed, polymerization from dilute aqueous solutions has not been concerned in the reported polymerizable anionic gemini surfactant system\(^15\). The aim of our current work is, therefore, to understand interfacial adsorption, micellization and subsequent polymerization of our novel polymerizable anionic gemini surfactant. Two comparative surfactants (i.e. a conventional anionic gemini one and a polymerizable anionic monomeric one) have also been employed in this study in order to elucidate interfacial properties of the polymerizable anionic gemini surfactant.

### 2 EXPERIMENTAL

#### 2.1 Materials

The following chemicals were used for surfactant syntheses: ethylenediamine (Wako Pure Chemical Industries Ltd.), 1,3-propanesultone (Wako), 12-hydroxydecanoic acid (Aldrich), methacryloyl chloride (Tokyo Chemical Industry Co. Ltd., TCI), oxalyl chloride (TCI), lauroyl chloride (TCI), N-methyltaurine (Wako) and 2,5-bis(1,1,3,3-tetramethylbutyl)hydroquinone (TCI). The other chemicals including NaOH, NaCl, HCl, pyridine, tetrahydrofuran, diethyl ether, acetone, chloroform, ethyl acetate, methanol and hexane were purchased from Wako. The chemicals listed above were of analytical grade and used without further purification.

The water used in the current study was filtered with a Millipore membrane filter (0.22 μm in pore size) after deionization with a Barnstead NANO pure diamond UV system.

#### 2.2 Synthesis

##### 2.2.1 Polymerizable anionic gemini surfactant: PA12-2-12

The polymerizable anionic gemini surfactant was obtained via the reaction of \(\text{N},\text{N}'\text{-dipropanesulfonyl ethylenediamine} (I)\) with methacryloyloxydecanyl chloride (II). In the following section, we first present the synthesis of these two materials (see also Fig. 1).

\(\text{N,N}'\text{-dipropanesulfonyl ethylenediamine} (I)\) was obtained via the reaction of ethylenediamine with 1,3-propanesultone. Ethylenediamine (18 g, 0.3 mol) was mixed with 200 cm\(^3\) of water and then 1,3-propanesultone (110 g, 0.9 mol) was added dropwise to this aqueous solution under ice-cooling. The mixture was stirred for 2 h under ice-cooling. After this reaction, ethanol was added to this mixture and then the ethanol mixture was stored overnight under ice-
cooling. The precipitates obtained here were recrystallized 5 times with an ethanol-water mixture. The yield of the crystalline product, obtained here after vacuum drying, was 62%.

Methacryloyloxydodecanyl chloride (II) was synthesized via the following two steps. In the first reaction step, 12-hydroxydodecanoic acid (25 g, 0.11 mol) was dissolved in tetrahydrofuran (100 cm³) with pyridine (10.1 g, 0.13 mol) and 2,5-bis(1,1,3,3-tetramethylbutyl)hydroquinone (0.16 g, 0.00048 mol). Under ice-cooling, methacryloyl chloride (13.3 g, 0.13 mol) was added dropwise to the tetrahydrofuran solution and the mixture was reacted for 5 h at room temperature. After this chemical reaction, insoluble pyridine-HCl salts were removed by filtration and then the solvent was evaporated. The product obtained here (i.e., methacryloyloxydodecanyl acid) was extracted with diethyl ether from a 5% HCl aqueous solution (in order to remove pyridine from the reaction system). The organic phase was again evaporated and the residue was purified with column chromatography (silica gel C-100, the eluting solution was a hexane-ethyl acetate mixture (2:1 in volume)). After this purification and subsequent drying, a phlegmatic light-yellow product was obtained in a ~70% yield. In the subsequent second stage, oxalyl chloride (41.2 g, 0.33 mol) was added dropwise to methacryloyloxydodecanyl acid (23.5 g, 0.083 mol) under ice-cooling. The mixture was reacted for 3 h at room temperature, and then it was evaporated under reduced pressure in order to remove unreacted oxalyl chloride. Methacryloyloxy-dodecanyl chloride (II) was obtained in a 70% yield at this second stage.

For the final synthesis of PA12-2-12, N,N'-dipropanesulfonyl ethylenediamine (I) (10 g, 0.033 mol) was dissolved in a mixture of water and acetone (7:3 in volume, 200 cm³) with 2,5-bis(1,1,3,3-tetramethylbutyl) hydroquinone (0.16 g, 0.00048 mol). An NaOH aqueous solution was added dropwise to this mixture and the solution pH was adjusted to 9-10. Under ice-cooling, methacryloyloxydodecanyl chloride (II) (22.1 g, 0.066 mol) was added dropwise to this alkaline solution. We note that the solution pH was always fixed in the range of 7.5-10 during this reaction stage, by adding the NaOH solution. The reaction mixture was stirred for 24 h and then the solvent was removed by freeze drying. The product obtained here was light-yellow and crystalline. The product was purified with column chromatography (silica gel C-100, the eluting solution was either a mixture of hexane and ethyl acetate (2:1 in volume) or a mixture of chloroform and methanol (5:2 in volume)). After this purification and subsequent removal of the solvent, the product became white and crystalline. The yield of this chemical reaction (including the purification) was 15%.

The final product was characterized with FT-IR spectroscopy (JASCO FT-IR 6100), 1H NMR spectroscopy (JEOL JNM-AL 300 MHz or JEOL JNM-ECP 500 MHz), FAB-Mass spectroscopy (JEOL JMS-SX102A) and elemental analysis (Perkin-Elmer 2400II CHNS/O). The FT-IR, LR-MS and elemental analysis data are shown below and the purity of PA12-2-12 is discussed in the Results and Discussion section on the basis of 1H NMR data.

FT-IR (KBr): 1715 cm⁻¹ (C=O), 1653 cm⁻¹ (C=N) and 1186 cm⁻¹ (S=O).

LR-MS: [M-Na]⁻ m/z found, 857 (calcd. 857.4).

Elemental analysis: PA12-2-12 calculated for C₄₀H₇₀N₂O₁₂S₂Na₂·H₂O: C, 53.44; H, 8.07; N, 3.11.

Fig. 1 Synthetic Routes of the Anionic Surfactants Employed in This Study.
2.2.2 Conventional anionic gemini surfactant: A12-2-12

\(N, N'\)-dipropanesulfonylethylendiamine (I) (8 g, 0.026 mol) was first dissolved in a mixture of water and acetone (7:3 in volume, 200 cm\(^3\)). An NaOH aqueous solution was added dropwise to this mixture and the solution pH was adjusted to 9 - 10. Under ice-cooling lauroyl chloride (12.5 g, 0.057 mol) was added dropwise to this alkaline solution. We note that the solution pH was always fixed in the range of 7.5 - 10 during this reaction stage, by adding the NaOH solution. The reaction mixture was stirred for 24 h and then the solvent was removed by freeze drying. The product obtained here was white and crystalline. The product was purified with column chromatography (silica gel C-100, the eluting solution was a mixture of chloroform and methanol (5:2 in volume)). Finally, the product obtained after this purification was further recrystallized 5 times from a mixture of tetrahydrofuran and water. The yield of this chemical reaction (including the purification) was 30%.

FT-IR (KBr): 1632 cm\(^{-1}\) (\(\equiv\)O) and 1184 cm\(^{-1}\) (S=O).

\(^1\)H NMR (CD\(_3\)OD): \(\delta\) 0.90 (t, 6H, 2CH\(_3\)), 1.29 (m, 32H, 2CH\(_2\)-), 1.58-1.59 (m, 4H, 2-CH\(_2\)-CON-), 2.04 (m, 4H, 2-CH\(_2\)-CON-), 2.33-2.44 (m, 4H, 2N-CH\(_2\)-CH\(_2\)-SO\(_3\)Na), 2.77-2.84 (m, 4H, 2N-CH\(_2\)-CH\(_2\)-SO\(_3\)Na) and 3.32-3.57 ppm (m, 6H, 2-CH\(_2\)-SO\(_3\)Na, CO-N-CH\(_2\)-CH\(_2\)-N-CO).

LR-MS: [M-Na]\(^{-}\) m/z found. 689 (calcd. 689.4).

Elemental analysis: PA12 calculated for \(C_{19}H_{34}N_{1}O_{6}S_{1}Na_{1}\): C, 53.38; H, 8.02; N, 3.28. Found: C, 53.31; H, 8.82; N, 2.95.

2.2.3 Polymerizable anionic monomeric surfactant: PA12

\(N\)-methyltaurine (10.4 g, 0.075 mol) was dissolved in a mixture of water and acetone (7:3 in volume, 200 cm\(^3\)) with 2,5-bis(1,1,3,3-tetramethylbutyl) hydroquinone (0.16 g, 0.00048 mol). An NaOH aqueous solution was added dropwise to this mixture and the solution pH was adjusted to 9 - 10. Under ice-cooling methacryloyloxydodecanyl chloride (12.5 g, 0.057 mol) was added dropwise to this alkaline solution. We note that the solution pH was always fixed in the range of 7.5 - 10 during this reaction stage, by adding the NaOH solution. The reaction mixture was stirred for 24 h and then the solvent was removed by freeze drying. The product obtained here was white and crystalline. The yield of this chemical reaction (including the purification) was 14%.

FT-IR (KBr): 1719 cm\(^{-1}\) (\(\equiv\)O), 1639 cm\(^{-1}\) (\(\equiv\)O/N) and 1186 cm\(^{-1}\) (S=O).

\(^1\)H NMR (CD\(_3\)OD): \(\delta\) 1.47-1.58 (m, 3H, -CH\(_2\)-), 1.92 (s, 3H, CH\(_3\) = CCH\(_3\)), 2.33-2.44 (m, 2H, -CH\(_2\)-CON-), 2.92-3.10 (m, 5H, N-CH\(_2\)-N-CH\(_2\)-CH\(_2\)-SO\(_3\)Na), 3.74 (t, 2H, -CH\(_2\)-SO\(_3\)Na), 4.13 (t, 2H, COOCH\(_2\)-), 5.59 and 6.06 ppm (s, 2H CH\(_2\) = CCH\(_3\)).

LR-MS: [M-Na]\(^{-}\) m/z found. 404 (calcd. 404.2)

Elemental analysis: PA12 calculated for \(C_{19}H_{34}N_{1}O_{6}S_{1}Na_{1}\): C, 53.88; H,8.02; N, 3.28. Found: C, 53.21; H, 8.82; N, 2.95.

2.3 Measurements

Aqueous surfactant solutions were prepared via direct dissolution of the powdered samples in the presence of added electrolytes at their desired concentrations. For all the surfactants used in this work, neither precipitation nor phase separation was seen in a whole range of concentrations investigated. All measurements reported here 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. The measurements were continued until a change in the surface tension becomes less than 0.1 mN m\(^{-1}\) per 15 min.

In order to estimate the micro-environmental polarity of the micelle interiors, steady-state fluorescence measurements were performed with a Shimadzu RF-5300PC fluorescence spectrophotometer using pyrene as a fluorescence probe. The spectrum was recorded between 360 and 400 nm with the excitation wavelength of 335 nm. The concentration of pyrene was set to approximately 1 \(\mu\)mol dm\(^{-3}\). As well known\(^{16,17}\), the fluorescence intensity ratio of the first (373 nm) to the third (384 nm) vibrational peaks \(I_3/I_1\) indicates the micro-environmental polarity around the pyrene molecules: the decrease in the \(I_3/I_1\) value is indicative of formation of the more hydrophobic environments. In our current study, we have determined the cmc of each surfactant under an assumption that the \(I_3/I_1\) value starts to decrease from the cmc when the surfactant concentration is increased.

For cryo-TEM measurements, the sample grid was prepared as follows: (i) a small amount of sample solutions was mounted on a TEM copper grid coated with a holey carbon film; (ii) the grid was mounted by a pair of self-locking tweezers; (iii) the excess amount of the sample solution was removed from the grid using a filter paper; and finally (iv) the grid was introduced into liquid ethane cooled by liquid nitrogen. The prepared grid was then set on the cryo-TEM holder under liquid nitrogen cooling. Cryo-TEM measurements were made using a Hitachi H-7650 at an accelerating voltage of 120 kV under a low electron dose.

Room temperature TEM (RT-TEM) measurements were carried out using the Hitachi H-7650 TEM, operated at an accelerating voltage of 120 kV. A small amount of sample
solutions was mounted on a TEM copper grid covered with a holey carbon film, and was dried in a desiccator for one day. Images were recorded digitally with a CCD camera.

3 RESULTS AND DISCUSSION

3.1 Molecular characteristics

Although the polymerizable anionic gemini surfactant (PA12-2-12) synthesized in this study gives reasonable FT-IR, LR-MS and elemental analysis data (see the Experimental section), the resultant 1H NMR data are somewhat complicated than we have expected. The results are summarized in Table 1, where the number of protons is calculated on the basis of 28 protons (2-(CH$_2$)$_7$-) observed at 1.31 ppm. The key finding is that the number of protons originated from the polymerizable methacryloxy groups (the total number of protons expected is 4 at 5.61 and 6.07 ppm) is decreased to 2.88, and instead, the sharp signal assigned as methylene groups appears at 1.48 ppm. This means that the methacryloxy groups covalently bound to the terminal of the hydrocarbon chains are somewhat polymerized during the synthesis. The purity of PA12-2-12 is estimated to be ca. 72% on the basis of the number of protons originated from the methacryloxy groups. Of course, we had tried to improve the purity of our sample, however, it was limited success because of the similar solubility of polymerized and unpolymerized (pure) samples to various solvents. It seems likely that the polymerization occurs within a molecule as a result of the condensation effect$^{14)}$ rather than between molecules, which may be rationalized by the fact that the corresponding polymerizable monomeric surfactant (PA12) is obtained with negligible impurities.

3.2 Interfacial Adsorption

Figure 2 shows the static surface tension of aqueous solutions of the polymerizable gemini surfactant (PA12-2-12), the conventional gemini surfactant (A12-2-12) and the polymerizable monomeric surfactant (PA12) as a function of their concentrations. In these measurements the background electrolyte ($NaCl$) concentrations were set at (a) 0 mmol dm$^{-3}$ and (b) 10 mmol dm$^{-3}$, respectively. For all the surfactants employed in this study, in the region of low surfactant concentrations the surface tension decreases sharply with increasing concentration and attains a break point. The surfactant concentration attained to this break point is assumed to be the cmc of each surfactant. The surface tension data shown in Fig. 2 allow us to calculate some physicochemical parameters (see Table 2): the surface tension measured at the cmc ($\gamma_{cmc}$), the surface excess concentration estimated at the cmc ($\Gamma_{cmc}$), the occupied area per surfactant molecule adsorbed at the air/aqueous solution interface ($A_{cmc}$), the standard free energy of micellization that occurs in bulk solution ($\Delta G_{mic}^{0}$) and the standard free energy of adsorption to the air/aqueous solution interface ($\Delta G_{ads}^{0}$)$^{18,19)}$.

$$\Gamma_{cmc} = -\frac{1}{iRT} \frac{d\gamma}{d\ln C} \quad (1)$$

Table 1  Summary of 1H NMR Data of PA12-2-12 (in CD$_3$OD).

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Assignment</th>
<th>Expected H number</th>
<th>Estimated H number$^{a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.31 (m)</td>
<td>2-(CH$_2$)$_7$-</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>1.58 – 1.69 (m)</td>
<td>2-COOCH$_2$CH$_2$-, 2-CH$_2$CH$_2$-CON-</td>
<td>8</td>
<td>8.47</td>
</tr>
<tr>
<td>1.48 (s)</td>
<td>2-CH$_2$-CHCH$_2$- (polymeric)</td>
<td>–</td>
<td>0.77</td>
</tr>
<tr>
<td>1.92 (s)</td>
<td>2CH$_2$=CCH$_3$</td>
<td>6</td>
<td>4.46</td>
</tr>
<tr>
<td>2.01 – 2.05 (m)</td>
<td>2N-CH$_2$CH$_2$SO$_3$Na,</td>
<td>4</td>
<td>4.10</td>
</tr>
<tr>
<td>2.36 – 2.44 (m)</td>
<td>2CH$_2$-CON-</td>
<td>4</td>
<td>4.13</td>
</tr>
<tr>
<td>2.76 (br)</td>
<td>2N-CH$_2$CH$_2$SO$_3$Na</td>
<td>4</td>
<td>4.02</td>
</tr>
<tr>
<td>3.49 – 3.59 (m)</td>
<td>2-CH$_2$SO$_3$Na, CO-N-CH$_2$-CH$_2$-N-CO</td>
<td>8</td>
<td>7.83</td>
</tr>
<tr>
<td>4.13 (t)</td>
<td>2COOCH$_2$-</td>
<td>4</td>
<td>3.84</td>
</tr>
<tr>
<td>5.61 (s)</td>
<td>CH$_2$=CCH$_3$</td>
<td>2</td>
<td>1.44</td>
</tr>
<tr>
<td>6.07 (s)</td>
<td>CH$_2$=CCH$_3$</td>
<td>2</td>
<td>1.44</td>
</tr>
</tbody>
</table>

$^{a)}$Calculated on the basis of 28 protons (2-(CH$_2$)$_7$-) observed at 1.31 ppm.
where $\gamma$ is the equilibrium surface tension measured at the surfactant concentration of $C$, $\gamma_0$ is the surface tension of pure water (or an aqueous electrolyte solution), $\omega$ is the molarity of water, $T$ is the absolute temperature, $N_A$ is the Avogadro’s number and $R$ is the gas constant. The degree of counter-ion binding to the micelle/aqueous solution interface ($\beta$) was determined by the Corrin-Harkins analysis\(^{20,21}\) and the detail is given later. Note that the numbers of adsorption species ($i$ in equation 1) have been assumed to be 3 in the absence of added electrolytes\(^{22}\) and 1 in the presence of excess amount of added electrolytes (10 mmol dm\(^{-3}\) NaCl), respectively. We also calculated the $pC_{20}$ value of each surfactant: the $C_{20}$ value is defined to be the surfactant concentration where a decrease in the surface tension by 20 mN m\(^{-1}\) from pure water (or an aqueous electrolyte solution) is recorded ($pC_{20} = -\log C_{20}$), and therefore, this value is indicative of an efficiency in lowering the surface tension\(^{18}\). In the following discussion, we compare the physicochemical parameters of the polymerizable gemini surfactant with the corresponding data of the conventional gemini and/or polymerizable monomeric ones, in order to elucidate complex nature of PA12-2-12.

First of all, it should be noted that the polymerizable terminal groups covalently bound to the hydrocarbon chains lead to (i) an increased intra- and inter-molecular repulsion, caused by conjugated double bonds of the polymerizable groups (in other words, the conjugated double bonds result in a decreased hydrophobicity of the surfactant molecule) and/or (ii) an increased hydrophobicity as a

$$A_{cmc} = \frac{1}{N_A \Gamma_{cmc}}$$

$$\Delta G_{ads}^0 = \Delta G_{mic}^0 = \left(\frac{\gamma_0 - \gamma_{cmc}}{\Gamma_{cmc}}\right)$$

Table 2 Physicochemical Properties of the Synthesized Surfactants.

<table>
<thead>
<tr>
<th></th>
<th>cmc</th>
<th>$\gamma_{cmc}$</th>
<th>$\Gamma_{cmc}$</th>
<th>$A_{cmc}$</th>
<th>$\Delta G_{mic}^0$</th>
<th>$\Delta G_{ads}^0$</th>
<th>$pC_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mmol dm(^{-3}) NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12-2-12</td>
<td>0.078</td>
<td>43.3</td>
<td>0.83</td>
<td>2.0</td>
<td>-19.9</td>
<td>-54.5</td>
<td>4.8</td>
</tr>
<tr>
<td>A12-2-12</td>
<td>0.31</td>
<td>41.1</td>
<td>0.88</td>
<td>1.9</td>
<td>-18.8</td>
<td>-54.0</td>
<td>4.3</td>
</tr>
<tr>
<td>PA12</td>
<td>0.16</td>
<td>41.1</td>
<td>1.8</td>
<td>0.93</td>
<td>-18.6</td>
<td>-35.7</td>
<td>4.4</td>
</tr>
</tbody>
</table>

|                  |     |                |                |           |                   |                   |           |
| 10 mmol dm\(^{-3}\) NaCl |     |                |                |           |                   |                   |           |
| PA12-2-12        | 0.053 | 42.3           | 1.3            | 1.2       | -20.4             | -43.3             | 5.6       |
| A12-2-12         | 0.12  | 40.8           | 1.5            | 1.1       | -20.3             | -41.1             | 5.3       |
| PA12             | 0.074 | 41.7           | 3.2            | 0.52      | -19.6             | -29.1             | 4.7       |

Fig. 2 Static Surface Tension of Aqueous Surfactant Solutions Measured (a) in the Absence Added Electrolytes and (b) in the Presence of 10 mmol dm\(^{-3}\) NaCl: PA12-2-12 (closed circles), A12-2-12 (open circles) and PA12 (closed triangles).
result of an increase in the total number of carbon atoms. This means that the interfacial properties would result from a balance of these two factors. When the second effect is predominant over the first one, the hydrophobicity of PA12-2-12 should be greater than that of A12-2-12, and therefore, the interfacial adsorption and subsequent molecular packing at the air/aqueous solution interface will be more pronounced for PA12-2-12 than for A12-2-12. This is partially supported by the interfacial parameters given in Table 2: for a given background electrolyte concentration, the presence of the polymerizable terminal group in the gemini structure results in a decreased cmc, an increased pCm, and negatively larger values of $\Delta G_{\text{mic}}^0$ and $\Delta G_{\text{ads}}^0$. All these parameters are primarily related with interfacial adsorption, and suggest that the adsorption to the air/aqueous solution interface is more pronounced for PA12-2-12 than for A12-2-12, as a result of an increased hydrophobic nature of PA12-2-12. The increased hydrophobic nature also results from the intra-molecular polymerization inducing a lack of relatively hydrophilic polymerizable groups.

It seems likely, on the other hand, that the first effect becomes predominant over the second one when the adsorbed PA12-2-12 molecules interact with each other and they form a monolayer film at the air/aqueous solution interface. As can be seen in Table 2, for both the background electrolyte concentrations (0 and 10 mmol dm$^{-3}$ NaCl), the polymerizable terminal group results in an increased $\chi_m$ and a slightly smaller $\Gamma_m$ (and hence a slightly larger $A_{\text{mic}}$) when compared with the data for the conventional gemini surfactant (A12-2-12). These are the opposite trend when taking the more hydrophobic nature of PA12-2-12 into consideration, and indicate the formation of a relatively less packed monolayer film of PA12-2-12 at the interface. This may result from the intra- and inter-molecular repulsion between the polymerizable terminal groups, caused by the relatively hydrophilic conjugated double bonds and/or their steric hindrance. In conclusion, the increased hydrophobicity due to the increased carbon number (and the intra-molecular polymerization) results in the pronounced interfacial adsorption of PA12-2-12, whereas the relatively hydrophilic nature (and/or the steric hindrance) of the polymerizable groups plays a significant role in the subsequent molecular packing at the interface.

As mentioned in the Introduction, the surface activity of gemini surfactants is generally greater than that of corresponding monomeric ones. This general trend is seen in our current case: for a given electrolyte concentration, PA12-2-12 gives a lower cmc, a larger pCm, and negatively larger $\Delta G_{\text{mic}}^0$ and $\Delta G_{\text{ads}}^0$ values than those for the corresponding monomeric surfactant PA12 (see Table 2). Interestingly, however, we also see a larger $\chi_m$ of PA12-2-12 than that of PA12, which is not in consistency with the greater surface activity of PA12-2-12. Again, this unexpected result suggests the formation of a less packed PA12-2-12 film at the air/aqueous solution interface. Here it should be noted that the $A_{\text{mic}}$ value of PA12-2-12 (gemini) is almost a double of the $A_{\text{mic}}$ value of PA12 (monomeric), although the occupied area per gemini surfactant molecule adsorbed at the interface is generally much smaller than a double of the $A_{\text{mic}}$ value of the corresponding monomeric surfactant (i.e., the adsorption to the interface occurs more effectively for gemini surfactants than for monomeric ones)[20]. The almost equivalent $A_{\text{mic}}$ values of PA12-2-12 and PA12 (per chain) suggest, therefore, that the degree of molecular packing at the interface (per chain) is more or less similar for the polymerizable surfactant systems (PA12-2-12 and PA12). We assume that the polymerizable terminal groups somewhat inhibit their close packing at the interface, overcoming the attractive molecular interaction that is frequently seen for gemini surfactants.

It was previously reported by Hamid and Sherrington[6] that the cationic monomeric surfactant modified with a polymerizable methacrylate group at the end of the hydrocarbon tail chain adopts a loop-like conformation at the air/aqueous solution interface (in which both ends of the surfactant molecule are located at the interface), as a result of a weak interaction of the polymerizable groups with water molecules. This molecular conformation leads to an extremely large occupied area per surfactant molecule adsorbed at the interface (1.13 nm$^2$ for the reported surfactant in the absence of added electrolytes). In our current case, there is no direct evidence confirming the chain conformation, however, we suggest the following possibilities: the relatively large $A_{\text{mic}}$ value of PA12-2-12 may result not only from the electrostatic repulsion between the anionic headgroups, but also from (i) the loop-like conformation of the two hydrophobic tail chains, or at least from (ii) the droop of the polymerizable terminal groups toward the solution surface.

Finally, we mention effects of added electrolytes on interfacial properties of the polymerizable gemini surfactant. In our current case, the addition of background electrolytes (10 mmol dm$^{-3}$ NaCl) results in a greater surface activity of the polymerizable gemini surfactant (i.e., lower cmc, lower $\chi_m$, greater $\Gamma_m$, smaller $A_{\text{mic}}$ and larger pCm, see Table 2). As is generally seen for many surfactant systems, this is rationalized by the fact that the added electrolytes shield the electrostatic repulsive interaction between ionic surfactant molecules both at the air/aqueous solution interface and in bulk solution, and hence the surface activity is increased in the presence of background electrolytes.

3.3 Micellization and Polymerization

Figure 3 shows the specific conductivity of (a) PA12-2-12, (b) A12-2-12 and (c) PA12 as a function of each surfactant concentration. These measurements were performed.
without added electrolytes. As is generally seen for many ionic surfactant systems, the specific conductivity is linearly increased with increasing surfactant concentration. For all the surfactants employed in this study, the slope of the conductivity against the surfactant concentration is slightly changed around the cmc of each surfactant, determined with static surface tensiometry. It is well known that such an inflection point seen in the specific conductivity data results from counter-ion binding to the micelle surface, and hence, it is possible to estimate the degree of micelle dissociation (α) by calculating the slope ratio below and above the inflection point. In the current case the α values are calculated to be 0.93 for PA12-2-12, 0.91 for A12-2-12 and 0.91 for PA12, respectively.

These relatively large dissociation degrees are also suggested by the Corrin-Harkins analysis: it is known that an electrolyte concentration is related with the cmc in accordance with the following equation:

$$\log \text{cmc} = -n\beta \log \frac{[\text{Na}^+]}{n} + \text{const}$$

where β is the degree of counter-ion binding to the micelle surface (β is defined as a ratio of the number of counter-ions adsorbed on the micelle surface to the micelle aggregation number of surfactants, β = 1 - α) and n is the number of counter-ions per surfactant molecule (i.e., n = 1 for monomeric and n = 2 for gemini surfactants). On the basis of this relationship, the nβ value (and hence the α value) is calculated as a slope of logarithmic cmc against logarithmic [Na+] / n. In Fig. 4 the cmc values determined from either static surface tensiometry or fluorescence I/I₀ measurements (see Experimental section) are plotted as a function of [Na⁺] / n in their logarithmic format. For all the surfactants studied here, in the lower [Na⁺] / n region the (logarithmic) cmc value is decreased gradually with increasing electrolyte concentration. Then, the slope in the log cmc against log [Na⁺] / n becomes always steeper when the electrolyte concentration is increased further. In accordance with the Corrin-Harkins analysis, the presence of such a break in the curve suggests a structural transformation to occur as a function of counter-ion concentration, reflecting a change in the dissociation degree of counter-ions from the micelle/aqueous solution interface. In our case we
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assume that the gradual decrease in the cmc observed in the lower [Na+/n] region corresponds to the formation of spherical micelles in bulk solution, whereas the steep decrease observed in the higher [Na+/n] region means the formation of non-spherical micelles as a result of the structural transformation. In the suggested spherical micelle region, the \( \alpha \) values are calculated to be 0.93 for PA12-2-12, 0.90 for A12-2-12 and 0.94 for PA12, respectively, which are in good consistency with the \( \alpha \) values determined from the conductivity measurements. The large \( \alpha \) values determined here may suggest the formation of loosely packed micelles in aqueous solutions.

We have performed polymerization of the polymerizable anionic gemini surfactant in the absence of added electrolytes at the concentration well above the cmc (1 mmol dm\(^{-3}\)). Before this polymerization, the spherical micelles suggested by the Corrin-Harkins analysis have been characterized with cryo-TEM measurements. Figure 5a shows a typical cryo-TEM image of PA12-2-12, observed at 1 mmol dm\(^{-3}\) PA12-2-12 in the absence of added electrolytes. In this image one can see spherical assemblies with an average diameter of 7.7 nm (see the size distribution histogram given in Fig. 5b).\(^4\) The micelle shape has been rationalized by the critical packing parameter (CPP)\(^4\), although exact calculation of CPP is a challenging work. In our current case it is possible to estimate the CPP value of PA12-2-12 under the assumptions that (i) each hydrophobic tail chain is long enough to allow the minimum cross-sectional area of it (i.e. \( v/lc \approx 0.21 \text{ nm}^2 \)); (ii) the total volume of the hydrophobic gemini chains is a double of the monomeric one; and (iii) the cross-sectional area of the gemini surfactant is equal to the occupied area of the surfactant molecule adsorbed at the air/aqueous solution interface, estimated from static surface tensiometry. By using the surface tension data (see Table 2), the CPP value of PA12-2-12 is calculated to be 0.21 in the absence of added electrolytes. This calculation indicates that the gemini surfactant favorably forms spherical micelles in the absence of added electrolytes. Clearly, this supports the experimental results shown in Fig. 5.

The spherical assemblies observed in the absence of added electrolytes have been polymerized by UV light irradiation (\( \lambda = 250 - 390 \text{ nm, } 100 \text{ mW cm}^{-2} \)) for 2 h in a 1 cm quartz cuvette under magnetic stirring. The surfactant concentration was set at 1 mmol dm\(^{-3}\) (well above the cmc), as mentioned above. We note here that (i) the polymerization was confirmed by disappearance of characteristic vinyl signals in the \(^1\text{H-}\text{NMR spectra (data not shown)}\) and (ii) neither precipitation nor phase separation was visually seen even after this polymerization. Figure 6a shows a cryo-TEM image of the polymerized assemblies, where one can still see spherical assemblies with an average diameter of 6.7 nm (see the size distribution histogram given in Fig. 6b). This result is supported by a high-resolution RT-TEM image (Fig. 6c), although the polymerized assemblies observed with RT-TEM are somewhat smaller than those with cryo-TEM. It should be emphasized, however, that no

\(^4\): It seems that the micelle size estimated by the cryo-TEM measurements is somewhat larger than we have expected as a core-shell type conventional surfactant micelle. This may result from the possibility that the cryo-TEM image was obtained in the 'underfocus' state and hence the observed micelles look larger than the real micelle size (cryo-TEM measurements are generally performed in the 'underfocus' state in order to obtain a high resolution image).
significant change in the micelle size is induced by this polymerization (based on the cryo-TEM data). This is a good piece of evidence that the spherical micelles spontaneously formed in aqueous solution play a key role for determining a structure of polymerized assemblies even if molecular exchange from/into the non-polymerized micelles occurs during the polymerization. Finally, we note that this experimental finding is in good consistency with our earlier report focusing on polymerization of a cationic gemini surfactant in the spherical micelle region.

4 CONCLUSIONS

In this article, we have presented the interfacial adsorption, micellization and subsequent polymerization of our novel polymerizable anionic gemini surfactant (PA12-2-12). On the basis of the static surface tension data, it seems likely that, when compared with a conventional anionic gemini surfactant (A12-2-12), (i) the interfacial adsorption of PA12-2-12 occurs more effectively from the low surfactant concentration region, whereas (ii) a weak interaction of the polymerizable terminal groups with water molecules (and/or the steric hindrance of the polymerizable groups) plays a significant role in the subsequent molecular packing at the air/aqueous solution interface. The latter effect (as well as the electrostatic repulsion between anionic headgroups) does inhibit their close packing, overcoming the strong intermolecular attractive interaction that is frequently seen for many gemini surfactant systems.

In the region of low added electrolyte concentrations, spherical micelles are spontaneously formed in the PA12-2-12 aqueous solution, which is confirmed with the Corrin-Harkins analysis and cryo-TEM measurements. Indeed
the spherical PA12-2-12 micelles are polymerized by UV light irradiation without any dramatic change in their original morphology. It is expected, therefore, that the polymerizable anionic gemini surfactant synthesized in this study is useful not only in developing nano-structural organic templates in aqueous solution but also in fabricating thin polymer films formed at various interfaces with enhanced kinetic and mechanical stability.

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