pH-regulated surface property and pH-reversible micelle transition of a tertiary amine-based gemini surfactant in aqueous solution

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Synthesis

Synthesis of compound 1

Aliphatic acid (0.2 mol) was added into a three-necked flask equipped with condenser and heated to 65 °C by oil bath. Quantitative thionyl chloride (33.8 g, 0.28 mol) was added dropwise under magnetic stirring once the aliphatic acid was melted completely. The released HCl and SO$_2$ were absorbed by diluted NaOH solution. Then the temperature was increased to 90 °C and 1.6 g I$_2$ was added as catalysis (0.5 h). The Br$_2$ (38.9 g, 0.24 mol) was added dropwise under magnetic stirring and reacted for 6 h. Then 30 mL of CH$_3$OH was gradually added under magnetic stirring at 55 °C. After the reaction products were cooled to room temperature, enough NaHSO$_3$ solution was added and a phase separation appeared. The organic layer was washed with 70 mL of water for 3 times and dried with anhydrous MgSO$_4$ overnight. Finally, the compound 1 was obtained as colorless oil.

Synthesis of compound 2

The mixture of acetone (80 mL) and K$_2$CO$_3$ (30.5 g, 0.22 mol) was heated to 60 °C under N$_2$ atmosphere. Quantitative hydroquinone (6.2 g, 0.05 mol) was added into the above mixture and magnetic stirring for 0.5 h. Then the compound 1 (60 g) was gradually added under magnetic stirring and the mixture was reacted for 48 h at 60 °C. The reaction products were separated by filtration and the filter cake was washed with 30 mL acetone for 3 times. The acetone in the filtrate was removed by rotary evaporation. The remaining solid was dissolved in 30 mL of CH$_2$Cl$_2$, and washed with NaOH solution (2 wt%) and water successively. Then crude product was gained by eliminating CH$_2$Cl$_2$ through rotary evaporation. Finally, the compound 2 as yellow powder was obtained by recrystallization from petroleum ether for 3 times.
Synthesis of \( C_m\)-A-C\(_m\)

The mixture of compound 2 (0.022 mol) and N,N'-dimethyl-1,3-propanediamine (8.9 g, 0.087 mol) was refluxed under nitrogen atmosphere and magnetic stirring for 24 h. The residual N,N'-dimethyl-1,3-propanediamine was removed by vacuum distillation. Then the remaining solid was recrystallized from n-heptane for 3 times, and the crude product was gained. The crude product was dissolved in CCl\(_4\) and the insoluble impurity was removed by filtration. The filtrate was extracted by dilute HCl aqueous solution. The white precipitate was generated when NaOH solution was gradually added into above aqueous solution. The finally surfactants, \( C_m\)-A-C\(_m\), were obtained as white powder by washing the precipitate with water for several times and removing the water in a vacuum oven successively. The final yield was 46% according to the quality of hydroquinone.

![Graphs](image-url)
**Fig. S1** TGA curves of (a) C₈-A-C₈, (b) C₁₀-A-C₁₀, (c) C₁₂-A-C₁₂, and (d) C₁₄-A-C₁₄.

**Table S1** The melting points (mp), decomposition temperature (dt), and element analyses of Cₘ-A-Cₘ

<table>
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<tr>
<th>Surfactant</th>
<th>mp (°C)</th>
<th>dt (°C)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
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<tr>
<td>C₈-A-C₈</td>
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<td>293</td>
<td>Calc. 68.9</td>
<td>10.5</td>
<td>8.9</td>
<td>10.2</td>
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<td>298</td>
<td>Calc. 71.1</td>
<td>11.0</td>
<td>8.3</td>
<td>9.5</td>
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<td></td>
<td></td>
<td></td>
<td>Found 71.2</td>
<td>10.8</td>
<td>8.2</td>
<td>9.2</td>
</tr>
<tr>
<td>C₁₂-A-C₁₂</td>
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<td>308</td>
<td>Calc. 72.2</td>
<td>11.2</td>
<td>7.7</td>
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<td></td>
<td>Found 72.1</td>
<td>11.6</td>
<td>7.5</td>
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<tr>
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<td>323</td>
<td>Calc. 73.2</td>
<td>11.4</td>
<td>7.1</td>
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<td>Found 72.9</td>
<td>11.4</td>
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**Fig. S2** (a) ¹H NMR (400 MHz, CDCl₃) and (b) ¹³C NMR (100 MHz, CDCl₃) of C₈-A-C₈.
Fig. S3 (a) $^1$H NMR (400 MHz, CDCl$_3$) and (b) $^{13}$C NMR (100 MHz, CDCl$_3$) of C$_{10}$-A-C$_{10}$.

Fig. S4 (a) $^1$H NMR (400 MHz, CDCl$_3$) and (b) $^{13}$C NMR (100 MHz, CDCl$_3$) of C$_{12}$-A-C$_{12}$.
Fig. S5 (a) $^1$H NMR (400 MHz, CDCl$_3$) and (b) $^{13}$C NMR (100 MHz, CDCl$_3$) of C$_{14}$-A-C$_{14}$.

Fig. S6 (a) pH titration curves of C$_{12}$-A-C$_{12}$ aqueous solutions (2 mM) in the presence of NaCl at 25 °C and (b) the corresponding differential curves calculated from the data of (a).
Fig. S7 Molecule state distributions of (a) C₈-A-C₈, (b) C₁₀-A-C₁₀, and (c) C₁₄-A-C₁₄ in aqueous solution varying with pH value.
Fig. S8 The steady state shear viscosity curves of the (a) C₈-A-C₈, (b) C₁₀-A-C₁₀, and (c) C₁₄-A-C₁₄ aqueous solutions (35 mM) at various pH values.
Fig. S9 (a, c and e) The dynamic oscillatory elastic ($G'$) modulus and viscous ($G''$) modulus varying with frequency and (b, d and f) Cole-Cole plot (solid line) of the C$_8$-A-C$_8$, C$_{10}$-A-C$_{10}$, and C$_{14}$-A-C$_{14}$ aqueous solutions (35 mM) at pH = 8.36, 7.35, and 6.04, respectively.