Supplementary Information

Wormlike Micelles and Gels Reinforced by Hydrogen Bonding in Aqueous Cationic Gemini Surfactant Systems

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Synthesis of 12-3-12, 12-3(OH)-12 and 14-3(OH)-14

1. The molecular structure of 12-3-12, 12-3(OH)-12 and 14-3(OH)-14 are shown as follows, starting materials: 1,3-dibromopropane (AR, Sinopharm Chemical Reagent Co., Ltd (China)),

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\begin{align*}
\text{CH}_3 & \text{N}^-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^-\text{CH}_3 \cdot 2\text{Br}^- & \text{CH}_3 & \text{N}^-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^-\text{CH}_3 \cdot 2\text{Br}^- \\
\text{C}_{12}\text{H}_{25} & \text{C}_{12}\text{H}_{25} & 12-3-12 & 12-3-12 \\
\text{CH}_3 & \text{OH} & \text{CH}_3 & \text{N}^-\text{CH}_2\text{CHCH}_2\text{N}^-\text{CH}_3 \cdot 2\text{Br}^- \\
\text{C}_{12}\text{H}_{25} & \text{C}_{12}\text{H}_{25} & 12-3\text{(OH)-12} & 12-3\text{(OH)-12} \\
\text{CH}_3 & \text{OH} & \text{CH}_3 & \text{N}^-\text{CH}_2\text{CHCH}_2\text{N}^-\text{CH}_3 \cdot 2\text{Br}^- \\
\text{C}_{14}\text{H}_{29} & \text{C}_{14}\text{H}_{29} & 14-3\text{(OH)-14} & 14-3\text{(OH)-14}
\end{align*}
\]

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glycerol (AR, Shanghai Chemistry Preparation Co., Ltd (China)), Amorphous phosphorus (CP, Dahao Fine & Special Chemical Products Company Shantou (China)), bromine (AR, Tianjin Fuchen Chemical Co., Ltd (China)), potassium permanganate (AR, Jinshan Xingta Chemical Co., Ltd (China)), N, N-Dimethyl dodecylamine (AR, Jiangsu Feixiang Chemical Co., Ltd (China)), N,N-Dimethyltetradecan-1-amine (AR, Jiangsu Feixiang Chemical Co., Ltd (China)), All these materials were used as received.

2. Synthetic routes

12-3-12:

\[
\begin{align*}
\text{Br} & \quad \text{Br} \quad \text{Br} \\
\text{(CH}_3\text{)}_2\text{NC}_{12}\text{H}_{25} & \quad \rightarrow \quad \text{C}_{12}\text{H}_{25}^+ \quad \text{N} \quad \text{N} \quad \text{C}_{12}\text{H}_{25}^+ \cdot 2\text{Br}^-
\end{align*}
\]

12-3(OH)-12:

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{P,Br}_2 \\
\text{Br} & \quad \text{OH} \quad \text{Br} \quad \text{(CH}_3\text{)}_2\text{NC}_{12}\text{H}_{25} \\
\text{HO} & \quad \text{OH} \\
\text{P,Br}_2 & \quad \rightarrow \\
\text{Br} & \quad \text{OH} \quad \text{Br} \quad \text{(CH}_3\text{)}_2\text{NC}_{12}\text{H}_{25} \\
\text{C}_{12}\text{H}_{25}^+ \quad \text{N} \quad \text{N} \quad \text{C}_{12}\text{H}_{25}^+ \cdot 2\text{Br}^-
\end{align*}
\]

14-3(OH)-14:

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{P,Br}_2 \\
\text{Br} & \quad \text{OH} \quad \text{Br} \quad \text{(CH}_3\text{)}_2\text{NC}_{14}\text{H}_{29} \\
\text{HO} & \quad \text{OH} \\
\text{P,Br}_2 & \quad \rightarrow \\
\text{Br} & \quad \text{OH} \quad \text{Br} \quad \text{(CH}_3\text{)}_2\text{NC}_{14}\text{H}_{29} \\
\text{C}_{14}\text{H}_{29}^+ \quad \text{N} \quad \text{N} \quad \text{C}_{14}\text{H}_{29}^+ \cdot 2\text{Br}^-
\end{align*}
\]

3. A detailed description about the synthesis

3.1 Synthesis of 12-3-12

This compound was synthesized with the method reported by Zana and Rosen et al.\textsuperscript{[1,2]}, which is briefly described as follows: 1,3-dibromopropane (5.0 g), N, N-Dimethyl dodecylamine (11.6 g) and absolute alcohol (50 ml) were added into the 250ml round bottom flask equipped with condenser tube. The mixture was stirred and heated to reflux for 48 h. The solvent was removed under reduced pressure to afford the viscous liquid with deep color. The crude product was first washed with absolute ether three times and then recrystallized from petroleum ether/acetone three
times to give 12-3-12 as white powder. Yield: 73.2%

3.2 Synthesis of 1, 3- dibromo-2-propanol

The method is briefly described as follows: Amorphous phosphorus (6.5 g) and glycerol (28.0 g) were added into the 250ml round bottom flask. The mixture was stirred by mechanical force. The bromine (52.8 g) was then slowly added with a temperature less than 80°C. This process took about 2 h and stirring was continued for another 2 h. Then the mixture was kept overnight. The saturated solution of sodium sulfite was added into the mixture to remove the residue bromine. The crude product was washed with saturated solution of sodium chloride three times and dried by anhydrous sodium sulfate. After vacuum distillation, 1, 3- dibromo-2-propanol was obtained as transparent and colorless liquid with the yield of 61.3%.

3.3 Synthesis of 12-3(OH)-12

The method was similar to that of 12-3(OH)-12. 1, 3- dibromo-2-propanol (5.0 g) and N,N-Dimethyl dodecylamine (13.8 g) were reacted to give 12-3(OH)-12 as white powder. Yield: 77.0%.

3.4 Synthesis of 14-3(OH)-14

The method was similar to that of 12-3(OH)-12. 1, 3- dibromo-2-propanol (5.0 g) and N,N-Dimethyltetradecan-1-amine (10.8 g) were reacted to give 14-3(OH)-14 as white powder. Yield: 82.5%.

4. NMR and elemental analysis of final products

12-3(OH)-12: $\delta_H$(400MHz, CDCl$_3$, TMS) 0.863-0.895 (t, 6H, CH$_3$), 1.255-1.360 (m, 36H, CH$_2$), 1.776-1.855 (m, 4H, CH$_2$), 3.462 (s, 12H, CH$_3$), 3.535-3.546 (t, 4H, CH$_2$), 3.630-3.684, 4.356 (m, 4H, CH$_2$), 5.248 (s, 1H, CH). Found: C, 57.1; H, 10.5; N, 4.35. Calc. for C$_{31}$H$_{68}$N$_2$Br$_2$O: C, 57.75; H, 10.6; N, 4.1%.
14-3(OH)-14: $\delta_H$ (400MHz, CDCl$_3$, TMS) 0.864-0.898(t, 6H, CH$_3$), 1.257-1.367(m, 40H, CH$_2$), 1.787-1.97,1.847-1.883(m, 8H, CH$_2$), 3.408-3.487 (s, 12H, CH$_3$), 3.487-3.530(t, 4H, CH$_2$), 3.674-3.731, 4.453-4.485(m, 4H, CH$_2$), 5.247-5.296(s, 1H, CH). Found: C, 59.6; H, 10.6 N, 4.1. Calc. for C$_{35}$H$_{76}$N$_2$Br$_2$O: C, 60.0; H, 10.9; N, 4.0%.

12-3-12: $\delta_H$ (400MHz, CDCl$_3$, Me$_4$Si) 0.861-0.905 (t, 6H, CH$_3$), 1.230-1.361 (m, 36H, CH$_2$), 1.786 (m, 4H, CH$_2$), 2.645-2.648 (m, 2H, CH$_2$), 3.399 (s, 12H, CH$_3$), 3.510-3.561 (m, 4H, CH$_2$), 3.781 (t, 4H, CH$_2$). Found: C, 59.4; H, 10.9; N, 4.3. Calc. for C$_{31}$H$_{68}$N$_2$Br$_2$: C, 59.2; H, 10.9; N, 4.5%.

References