Viscoelastic properties of supramolecular Gemini-like surfactant solutions in the absence of inorganic salts

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1. Synthesis of two compounds

The synthetic scheme of sodium Ph-C16 and N-2-N bromide are shown in Fig.S1

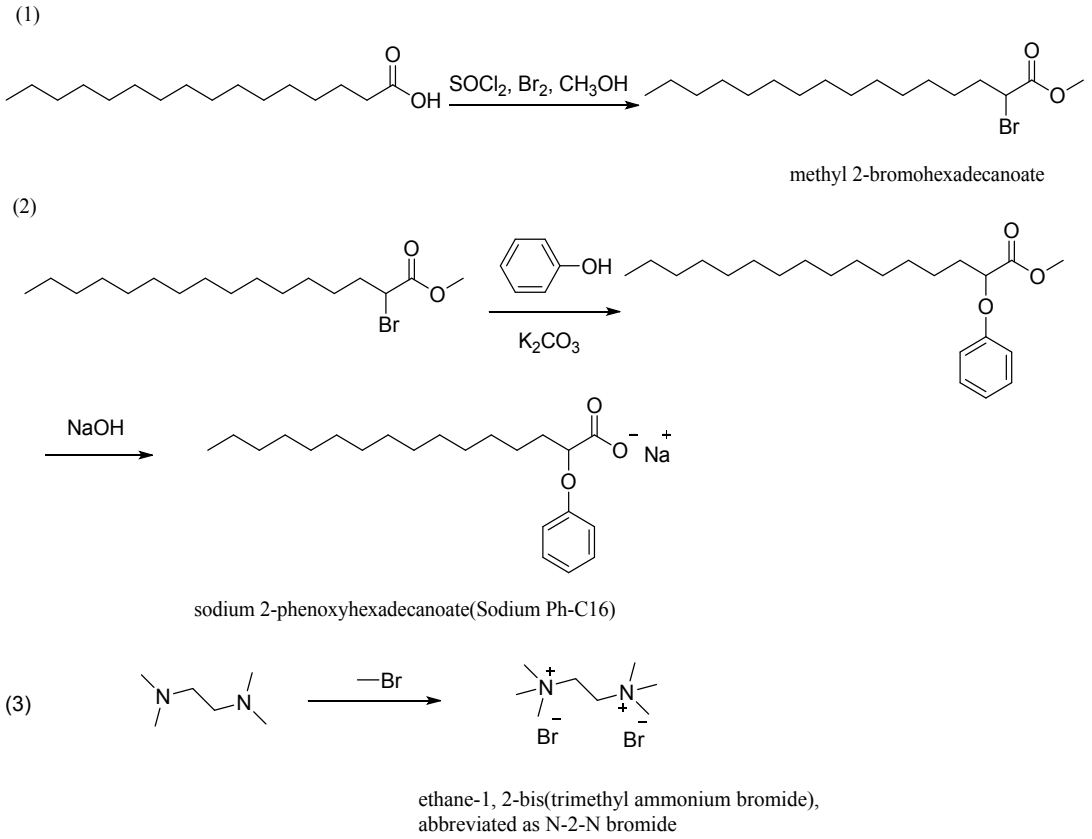

Fig.S1 The synthetic scheme of two compounds

1.1 Synthesis of methyl 2-bromohexadecanoate

The hexadecanoic acid (150 g, 0.58 mol) was added into a 500 mL three-necked flask. The temperature was raised to 65 °C until all solid dissolved. Thionyl chloride (95.1 g, 0.73 mol) was slowly added. The produced acidic gas was absorbed with NaOH solution. After the addition was

completed, the reaction was continued for another 3 hours at a temperature of 80°C. The temperature was then adjusted to 90°C and a catalytic amount of iodine was added. Bromine (116.6 g, 0.73 mol) was dropped in. This process shall take quite a long time to avoid the excessive loss of bromine. After all the bromine was added in, the reaction was continued for another 8 hours. The temperature was decreased to 65°C and methanol (73 g, 2.28 mol) was slowly added. The reaction was continued for 4 hours and the reaction mixture was cooled to room temperature. The deep-colored liquid was first rotated under reduced pressure and then washed with sodium sulfite solution. After the color became light, the liquid was washed with distilled water to pH = 7. After dried with anhydrous magnesium sulfate, the final product methyl 2-bromohexadecanoate was obtained by vacuum distillation. 195-200 °C /5mmHg. Yield: 73.1%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 2.15 – 1.91 (m, 2H), 1.45－1.26 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H).

1.2 Synthesis of sodium 2-phenoxyhexadecanoate (sodium Ph-C16)

The potassium carbonate (35.61 g, 0.2576 mol) and 80 mL DMF was added into a 500 mL three-necked flask. After stirring for 0.5 hours, phenol (20.4 g, 0.214 mol) dissolved in DMF was added in. The temperature was raised to 60 °C and stirring was continued for 1 hour. Methyl 2-bromohexadecanoate (30 g, 0.086 mol) was added and the temperature was raised to 80°C. The reaction was continued for another 12 hours. All processes were carried out under N_2 protection. After cooling, 20 mL H_2O cold water was added into the reaction mixture. The mixture was extracted three times with petroleum ether. The combined organic layer was washed three times with deionized water. After dried with anhydrous $MgSO_4$, the mixture was filtered to get the filtrate. The solvent was then removed under reduced pressure. The remaining crude product was further purified by column chromatography to give the pure methyl 2-phenoxyhexadecanoate. yield: 38.7%.

The sodium hydroxide (1.0 g, 0.025 mol), methyl 2-phenoxyhexadecanoate (8.3 g, 0.023 mol) and 200 mL ethanol were added into a 500 mL round-bottom flask. The reaction was carried out for 12 hours under 70 °C. When the reaction is completed, the solvent in the mixture was removed under reduced pressure. The residue was then recrystallized three times with ethanol. After dried under vacuum, the final product sodium 2-phenoxyhexadecanoate (sodium Ph-C16) was obtained as white solid. Yield: 87.2%.

^{1}H NMR (400 MHz, MeOD) δ 7.20 (t, *J* = 7.0 Hz, 2H), 6.90-6-80 (m, 3H), 4.35 (t, *J* = 6.3 Hz, 1H), 1.91-1.83 (m, 2H), 1.59-1.48 (m, 2H), 1.38-1.29 (m, 22H), 0.91 (t, *J* = 6.8 Hz, 3H).

Elemental analysis

Anal. Calcd. For $C_{22}H_{35}O_3Na$: C, 71.32; H, 9.52. Found: C, 71.48; H, 9.75.

1.3 Synthesis of ethane-1,2-bis(trimethyl ammonium bromide)(N-2-N bromide)

The *N*, *N*, *N*', *N*'-tetramethylethylenediamine (40 g, 0.33 mol) and 200 mL ethanol was added into an autoclave. The system was stored at -16°C for 3 hours. The already frozen methyl bromide (80.3 g, 0.84 mol) was quickly added and the autoclave was sealed. The reaction was carried out at 70°C for 6 hours. After the reaction mixture was cooled to room temperature, the solvent in the mixture was removed under reduced pressure. The crude product was recrystallized three times with methanol/ethanol mixed solvent. After drying, the final product was obtained as white solid. Yield: 58.5%.

^{1}H NMR (400 MHz, D_2O) δ 3.96-3.95(m, 4H), 3.23(s, 18H).

Elemental analysis

Anal. Calcd. for $C_8H_{22}Br_2N_2$: C, 31.39; H, 7.24; N, 9.15. Found: C, 31.26; H, 7.35; N, 8.97.

2. The steady shear viscosity of sodium Ph-C16 at 200 mmol·L^{-1} with the shear rates

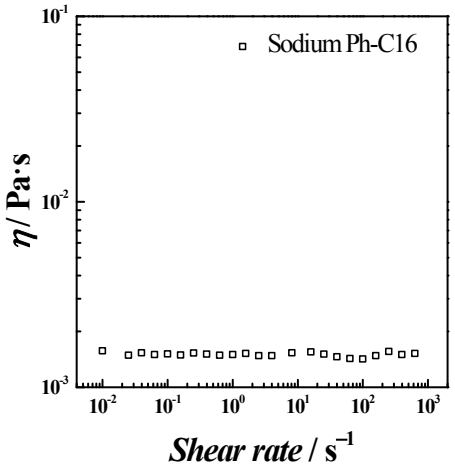

Fig.S2 Steady shear viscosity curve of sodium Ph-C16 at 200 mmol·L^{-1}

3. The steady shear viscosity of hexadecanoate/N-2-N system

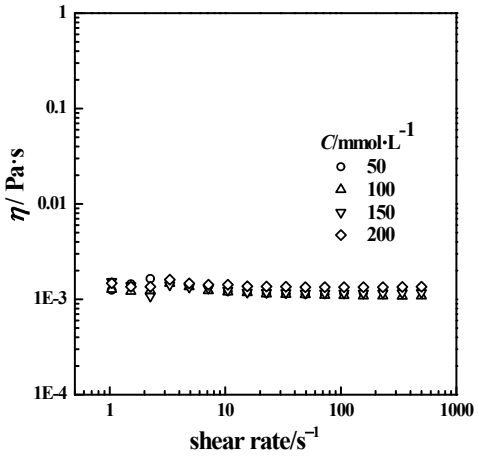

Fig.S3 Steady shear viscosity curves of hexadecanoate/N-2-N solutions at different hexadecanoate ion concentrations