Electronic Supplementary Material (ESI) for Soft Matter

Supplementary material

for

Adsorption and Micellization Behaviors of Gemini Surfactants with Pyrrolidinium Head Groups: Effect of the Spacer Length

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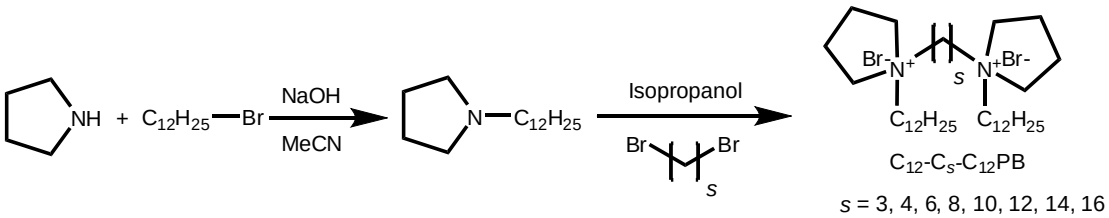


Scheme S1. The synthesis route of the Gemini surfactant C_{12}-C_s-C_{12}PB.

Scheme S1 shows the procedure for the synthesis of cationic Gemini surfactants with pyrrolidinium head groups, C_{12}-C_s-C_{12}PB. 1-Bromodecane (0.1mol) was firstly added to acetonitrile (50 ml) solution of pyrrolidine (0.12 mol) at room temperature at stirring. After that, sodium hydroxide and catalytic amount of potassium iodide was added to the above solution. The reaction mixture was stirred at reflux temperature for 48 hours. After the reaction finished, the solvent was removed by spinning evaporation. The residue was purified by flash column chromatography (silica, 1:3 EA/CH_2Cl_2, 0.5%$NH_3.H_2O$, R_f = 0.3), the colorless liquid products N-dodecyl pyrrolidine was obtained, yield 80%. Then, the obtained N-dodecyl pyrrolidine (0.08mol) was dissolved in 40 ml isopropanol in a 100 mL volume flask, and 1, s - dibromo butane (0.027 mol in 20ml isopropanol) was added gradually. The reaction mixture was stirred at reflux temperature for 48-96 hours. After removal of isopropanol, the product purified several times by recrystallized in the mixtures of ethanol/acetone (1:10). The products were characterized by employing ESI-MS (P/ACE MDQ), ^{1}HNMR spectra, ^{13}CNMR spectra (Mercury VX-300) in $CDCl_3$, and Element Analysis (VarioEL III). The results prove that they are all objective products.

(1) 1, 1'-(propane-1, 3- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_3-C_{12}PB)

White power, yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 36H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2), 2.14-2.40 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.68 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.26-4.01 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.36, 20.55, 22.74-22.90, 23.94, 26.68, 29.55-29.84, 32.12, 57.42, 61.21, 63.40. ESI-MS; [M-Br^-] $C_{35}H_{72}BrN_2^+$: Calcd: 599.4, Found: 599.3. Elemental analysis; Calcd(%): C, 61.75; H, 10.66; N, 4.11. Found: C, 60.83; H, 10.54; N, 3.97.

(2) 1, 1'-(butane-1, 4- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_4-C_{12}PB).

White power, yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 36H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2–N)), 2.20 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.62 (m, 4H, N-CH_2-**CH_2-CH_2**-CH_2-N), 3.26-4.01 (m, 16H, N-**CH_2**). ^{13}C NMR

(75 MHz, $CDCl_3$): δ = 14.45, 21.28, 23.00, 23.90, 26.88, 29.47-29.91, 32.21, 60.19, 61.26, 63.40. ESI-MS; [M-Br^-] $C_{36}H_{74}BrN_2^+$: Calcd: 613.5, Found: 613.3. Elemental analysis; Calcd(%): C, 62.23; H, 10.74; N, 4.03. Found: C, 61.07; H, 10.53; N, 3.98.

(3) 1, 1'-(hexane-1, 6- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_6-C_{12}PB).

White power, yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 36H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2, 4H, N–CH_2–CH_2–**$(CH_2)_2$**–CH_2–CH_2–N), 2.07 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.44 (m, 4H, N-CH_2-**CH_2**-CH_2-CH_2-**CH_2**-CH_2-N), 3.26-4.01 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.32, 22.28, 22.84, 23.70, 25.03, 26.65, 29.43-29.75, 59.70, 60.18, 63.21. ESI-MS; [M-Br^-] $C_{38}H_{78}BrN_2^+$: Calcd: 641.5, Found: 641.4. Elemental analysis; Calcd(%): C, 63.14; H, 10.88; N, 3.88. Found: C, 62.91; H, 10.64; N, 3.73.

(4) 1, 1'-(octane-1, 8- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_8-C_{12}PB).

White power, yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 44H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N, N–CH_2–CH_2–**$(CH_2)_4$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2–N), 2.20 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.62 (m, 4H, N–CH_2–**CH_2**–$(CH_2)_4$–**CH_2**–CH_2–N), 3.25-4.02 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.32, 22.25, 22.84, 23.72, 25.89, 26.36, 28.12, 29.48-29.75, 59.75, 60.31, 63.18. ESI-MS; [M-Br^-] $C_{40}H_{82}BrN_2^+$: Calcd: 669.5, Found: 669.3. Elemental analysis; Calcd(%): C, 63.98; H, 11.01; N, 3.73. Found: C, 63.54; H, 10.85; N, 3.59.

(5) 1, 1'-(decane-1, 10- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_{10}-C_{12}PB).

White power, yield: 77%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 48H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N, N–CH_2–CH_2–**$(CH_2)_6$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2–N), 2.20 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.52 (m, 4H, N–CH_2–**CH_2**–$(CH_2)_6$–**CH_2**–CH_2–N), 3.36-3.93 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.23, 22.12, 22.74, 23.63, 26.27, 26.49, 28.59, 28.79, 29.27-29.65, 31.95, 59.70, 59.95, 63.12. ESI-MS; [M-Br^-] $C_{42}H_{86}BrN_2^+$: Calcd: 697.6, Found: 697.4. Elemental analysis; Calcd(%): C, 64.76; H, 11.13; N, 3.60. Found: C, 64.52; H, 10.95; N, 3.48.

(6) 1, 1'-(dodecane-1, 12- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_{12}-C_{12}PB).

White power, yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 52H,

CH_3–**$(CH_2)_9$**–CH_2–CH_2–N, N–CH_2–CH_2–**$(CH_2)_8$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2–N), 2.20 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.42 (m, 4H, N–CH_2–**CH_2**–$(CH_2)_8$–**CH_2**–CH_2–N), 3.39-3.94 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.32, 22.15, 22.84, 23.77, 26.45, 29.08-29.75, 32.04, 59.70, 59.96, 63.20. ESI-MS; [M-Br^-] $C_{44}H_{90}BrN_2^+$: Calcd: 725.6, Found: 725.5. Elemental analysis; Calcd(%): C, 65.49; H, 11.24; N, 3.47. Found: C, 65.02; H, 11.06; N, 3.29.

(7) 1, 1'-(tetradecane-1, 14- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_{14}-C_{12}PB).

White power, yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 56H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N, N–CH_2–CH_2–**$(CH_2)_{10}$**–CH_2–CH_2–N), 1.79(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2–N), 2.10 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.32 (m, 4H, N–CH_2–**CH_2**–$(CH_2)_{10}$–**CH_2**–CH_2–N), 3.39-3.94 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.32, 22.12, 22.84, 23.71, 26.57, 29.34-29.75, 32.05, 59.68, 59.87, 63.22. ESI-MS; [M-Br^-] $C_{46}H_{94}BrN_2^+$: Calcd: 753.7, Found: 753.6. Elemental analysis; Calcd(%): C, 66.16; H, 11.35; N, 3.35. Found: C, 66.11; H, 11.08; N, 3.22.

(8) 1, 1'-(hexadecane-1, 16- diyl)bis(1-dodecyl pyrrolidinium) bromide (C_{12}-C_{16}-C_{12}PB).

White power, yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26 (m, 60H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N, N–CH_2–CH_2–**$(CH_2)_{12}$**–CH_2–CH_2–N), 1.75(m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2–N), 2.10 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.30 (m, 4H, N–CH_2–**CH_2**–$(CH_2)_{12}$–**CH_2**–CH_2–N), 3.39-3.94 (m, 16H, N-**CH_2**). ^{13}C NMR (75 MHz, $CDCl_3$): δ =14.30, 22.10, 22.82, 23.69, 26.53, 29.47-29.73, 32.03. ESI-MS; [M-Br^-] $C_{48}H_{98}BrN_2^+$: Calcd: 781.7, Found: 781.7. Elemental analysis; Calcd(%): C, 66.79; H, 11.44; N, 3.25. Found: C, 66.27; H, 11.22; N, 3.05.

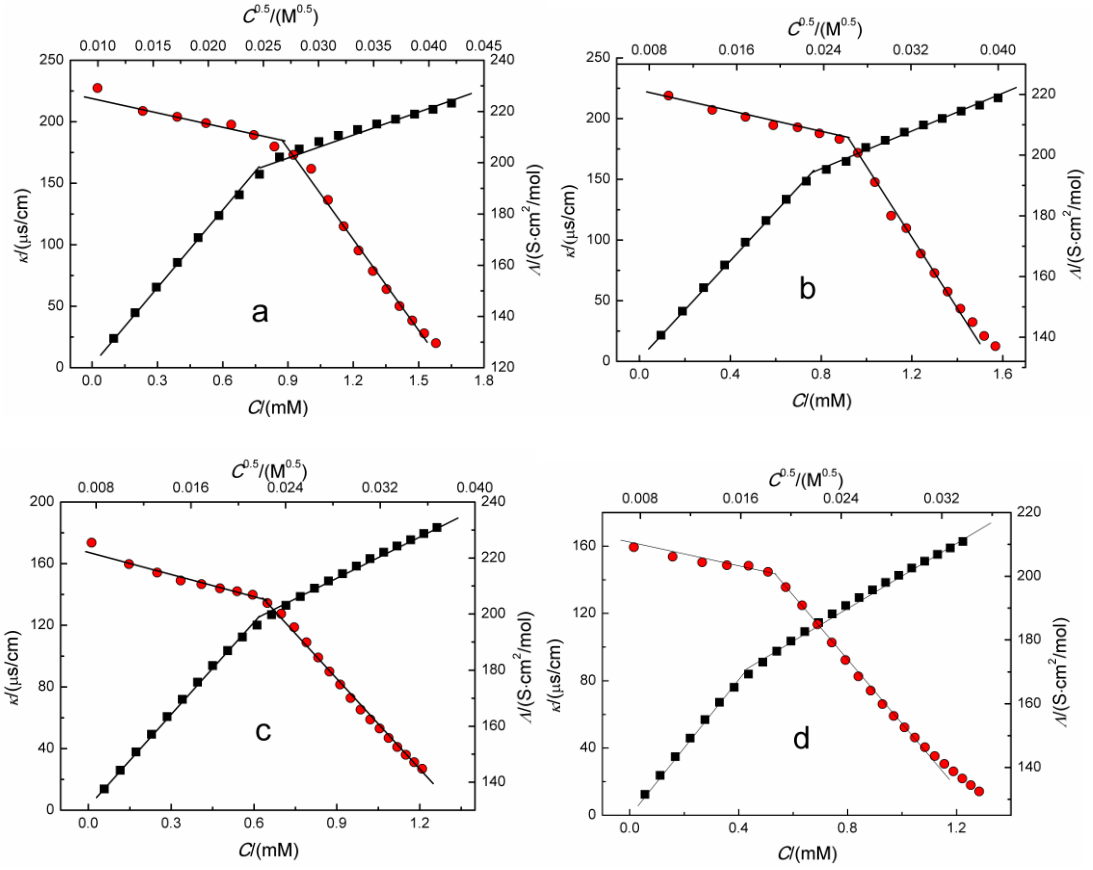
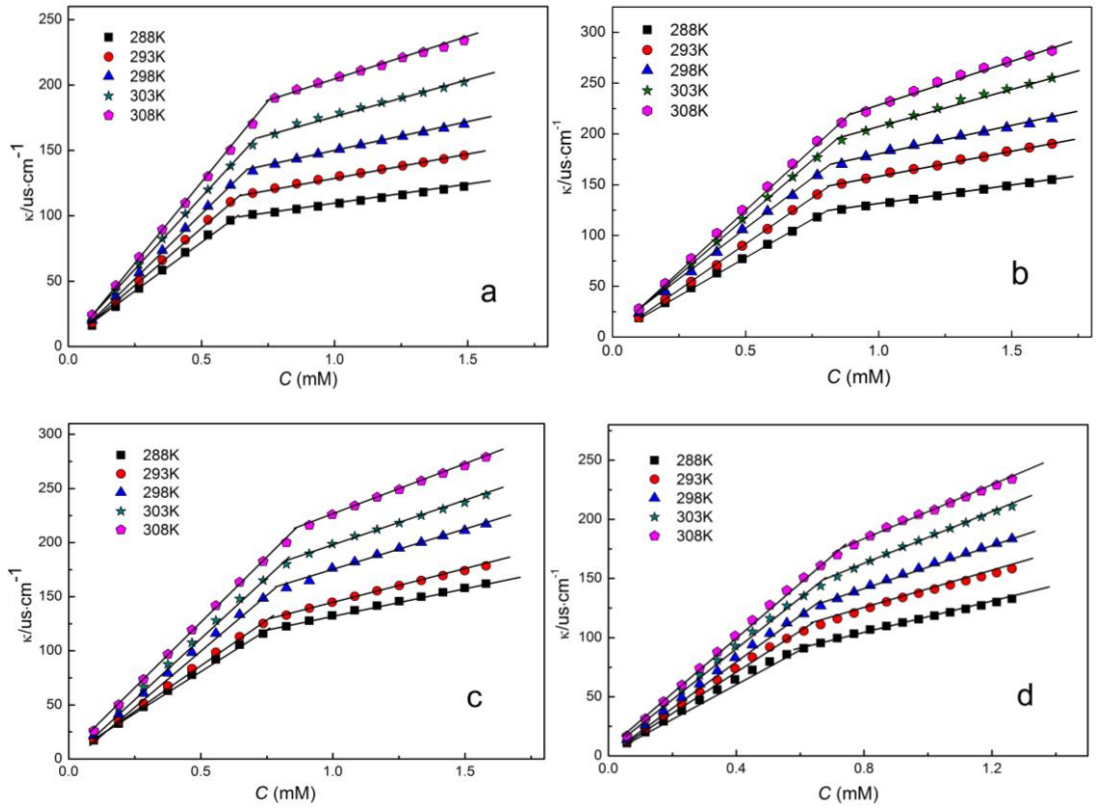


Figure S1. The κ~C and Λ~$C^{0.5}$ curves of C_{12}-C_4-C_{12}PB (a), C_{12}-C_6-C_{12}PB (b), C_{12}-C_8-C_{12}PB (c), C_{12}-C_{10}-C_{12}PB (d).



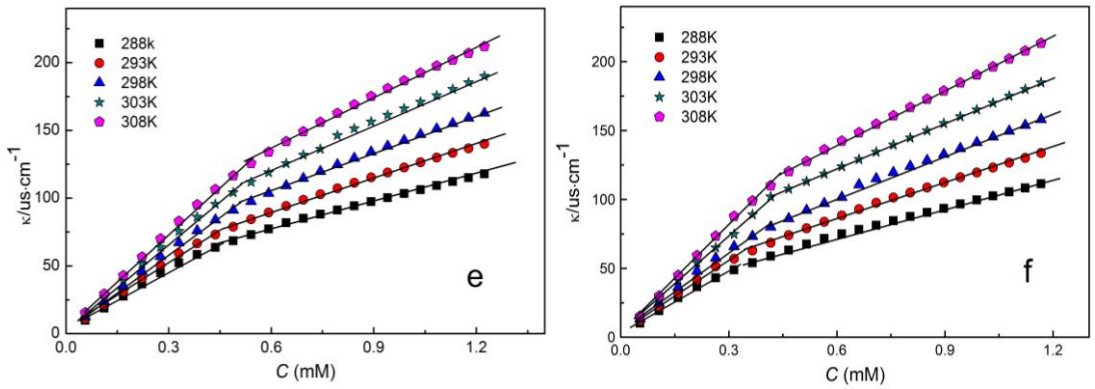


Figure S2. The κ~C curves of C_{12}-C_3-C_{12}PB (a), C_{12}-C_4-C_{12}PB (b), C_{12}-C_6-C_{12}PB (c), C_{12}-C_8-C_{12}PB (d), C_{12}-C_{10}-C_{12}PB (e) and C_{12}-C_{12}-C_{12}PB (f) at different temperature.