Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material

for

A Comprehensive Study on Micellization of Dissymmetric Pyrrolidinium Headgroups Based Gemini Surfactants

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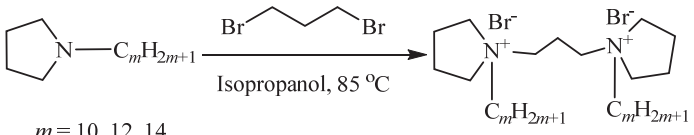
1. Synthesis of Gemini surfactants

Pyrrolidinium headgroups based Gemini surfactants are synthesized as Scheme S1.

a. Scheme for symmetric Gemini surfactants



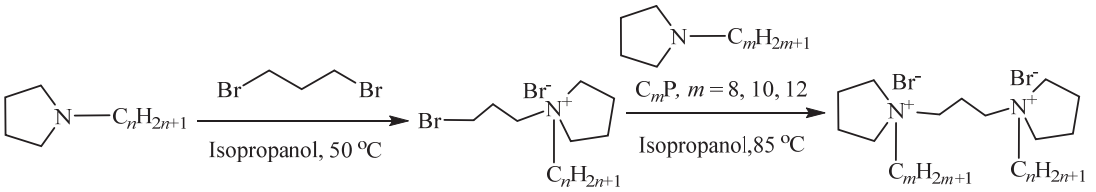
m = 10, 12, 14

$C_{10}C_3C_{10}$PB; m = 10

$C_{12}C_3C_{12}$PB; m = 12

$C_{14}C_3C_{14}$PB; m = 14

b. Scheme for dissymmetric Gemini surfactants



C_nP, n = 14, 16

C_nC_3PB, n = 14, 16

$C_{12}C_3C_{14}$PB; m = 12, n = 14

$C_{10}C_3C_{14}$PB; m = 10, n = 14

$C_8C_3C_{16}$PB; m = 8, n = 16

Scheme S1. The synthesis route of Gemini surfactants.

1.1 Synthesis of the symmetric Gemini surfactants

All N-alkyl pyrrolidine and the symmetric Gemini surfactants of $C_{10}C_3C_{10}$PB, $C_{12}C_3C_{12}$PB and $C_{14}C_3C_{14}$PB (Scheme S1a) are synthesized following the same procedure as that previously reported [1, 2].

$C_{10}C_3C_{10}$PB, white powder (yield: 83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26-1.42 (m, 28H, CH_3–**$(CH_2)_7$**–CH_2–CH_2–N), 1.77 (m, 4H, CH_3–$(CH_2)_7$–**CH_2**–CH_2), 2.15-2.40 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.61 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.54-4.02 (m, 16H, N-**CH_2**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.13, 20.29, 22.53-22.67, 23.74, 26.49, 29.30-29.50, 31.86, 57.22, 60.93, 63.26.

ESI-MS; [M-Br^-] $C_{31}H_{64}BrN_2^+$: Calcd: 543.4, Found: 543.3.

$C_{12}C_3C_{12}$PB, white powder (yield: 61 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26-1.44 (m, 36H, CH_3–**$(CH_2)_9$**–CH_2–CH_2–N), 1.78 (m, 4H, CH_3–$(CH_2)_9$–**CH_2**–CH_2), 2.15-2.41 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.64 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.50-4.02 (m, 16H, N-**CH_2**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.14, 20.30, 22.39-22.68, 23.79, 26.50, 29.35-29.64,

31.90, 56.84, 60.61, 63.26.

ESI-MS; [M-Br^-] $C_{35}H_{72}BrN_2^+$: Calcd: 599.4, Found: 599.3.

$C_{14}C_3C_{14}$PB, white powder (yield: 89 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.26-1.43 (m, 44H, CH_3–**$(CH_2)_{11}$**–CH_2–CH_2–N), 1.78 (m, 4H, CH_3–$(CH_2)_{11}$–**CH_2**–CH_2), 2.14-2.40 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.64 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.51-4.05 (m, 16H, N-**CH_2**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.16, 22.05, 22.71, 23.85, 26.38, 29.36-29.71, 31.93, 53.92, 60.04, 63.71.

ESI-MS; [M-Br^-] $C_{39}H_{80}BrN_2^+$: Calcd: 655.5, Found: 655.4.

1.2 Synthesis of the dissymmetric Gemini surfactants

The dissymmetric Gemini surfactants of $C_{12}C_3C_{14}$PB, $C_{10}C_3C_{14}$PB and $C_8C_3C_{16}$PB are synthesized according to Scheme S1b, the details are described as following: Firstly, 1, 3-dibromopropane (0.2 mol) is dissolved in 50 ml isopropanol in a 250 mL volume flask, and the solution of N-alkyl pyrrolidine (C_nP, n = 14 or 16; 0.1 mol) in 100 ml isopropanol is added gradually. The reaction mixture is stirred at 50 °C for 72 hours under N_2 atmosphere. After removal of isopropanol, the product is recrystallized in ethyl acetate twice and dried in vacuum for 72 hours to give white C_nC_3PB (n = 14 or 16; yield ~ 60 %). Then, 0.025 mol C_nC_3PB and 0.05 mol N-alkyl pyrrolidine (C_mP, m = 8, 10 or 12) is dissolved in 150 ml isopropanol in a 250 mL volume flask. The mixture is stirred at 85 °C for 72 hours under N_2 atmosphere. After removal of solvent, the product purified several times by recrystallized in the mixtures of ethanol/ethyl acetate (1/9, v/v) and dried in vacuum for 96 hours to give the pure Gemini surfactants.

$C_{12}C_3C_{14}$PB, white powder (yield: 44 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.25-1.41 (m, 36H, CH_3–**$(CH_2)_{11}$**–CH_2–CH_2–N and CH_3–**$(CH_2)_9$**–CH_2–CH_2–N), 1.77 (m, 4H, CH_3–$(CH_2)_{11}$–**CH_2**–CH_2 and CH_3–$(CH_2)_5$–**CH_2**–CH_2–N), 2.13-2.40 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.66 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.53-4.06 (m, 16H, N-**CH_2**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.14, 20.38, 22.63-22.70, 23.74, 26.48, 29.32-29.70, 31.92, 57.41, 61.23, 63.20.

ESI-MS; [M-Br^-] $C_{37}H_{76}BrN_2^+$: Calcd: 627.5, Found: 627.4.

$C_{10}C_3C_{14}$PB, white powder (yield: 53 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.25-1.41 (m, 36H, CH_3–**$(CH_2)_{11}$**–CH_2–CH_2–N and CH_3–**$(CH_2)_7$**–CH_2–CH_2–N), 1.77 (m, 4H, CH_3–$(CH_2)_{11}$–**CH_2**–CH_2 and CH_3–$(CH_2)_5$–**CH_2**–CH_2–N), 2.15-2.40 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.64 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.56-4.04 (m, 16H, N-**CH_2**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.14, 20.37, 22.57-22.70, 23.75, 26.49, 29.29-29.70, 31.92, 57.24, 61.09, 63.21.

ESI-MS; [M-Br^-] $C_{35}H_{72}BrN_2^+$: Calcd: 599.4, Found: 599.3.

$C_8C_3C_{16}$PB, white powder (yield: 32 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, **CH_3**), 1.25-1.41 (m, 36H, CH_3–**$(CH_2)_{13}$**–CH_2–CH_2–N and CH_3–**$(CH_2)_5$**–CH_2–CH_2–N), 1.76 (m, 4H, CH_3–$(CH_2)_{13}$–**CH_2**–CH_2 and CH_3–$(CH_2)_5$–**CH_2**–CH_2–N), 2.14-2.39 (m , 8H, N-CH_2-**CH_2** in pyrrolidine), 2.61 (m, 2H, N-CH_2-**CH_2** -CH_2-N), 3.54-4.02 (m, 16H, N-**CH_2**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.10, 20.34, 22.57-22.70, 23.76, 26.50, 29.13-29.71, 31.69-31.93, 57.26, 61.04, 63.26.

ESI-MS; [M-Br^-] $C_{35}H_{72}BrN_2^+$: Calcd: 599.4, Found: 599.3.

All the products are characterized by employing ^{1}H NMR spectra, ^{13}C NMR spectra in $CDCl_3$ (400 MHz Bruker-BioSpin spectrometer) and ESI-MS (P/ACE MDQ). The results confirm that they are the objective products.

2. Effect of the hydrophobic length and the dissymmetry on γ_{cmc} and A_{min}

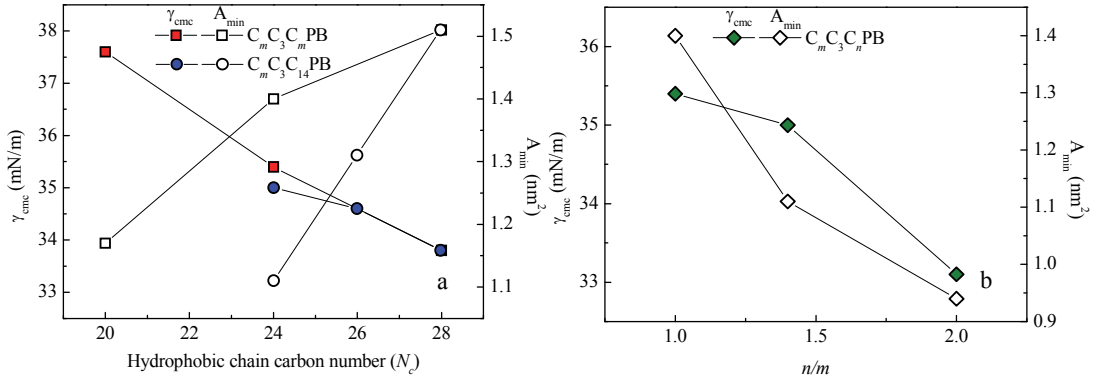


Figure S1. Effect of the hydrophobic length (a) and the dissymmetry (b) on γ_{cmc} and A_{min}.

3. Temperature dependent conductivities

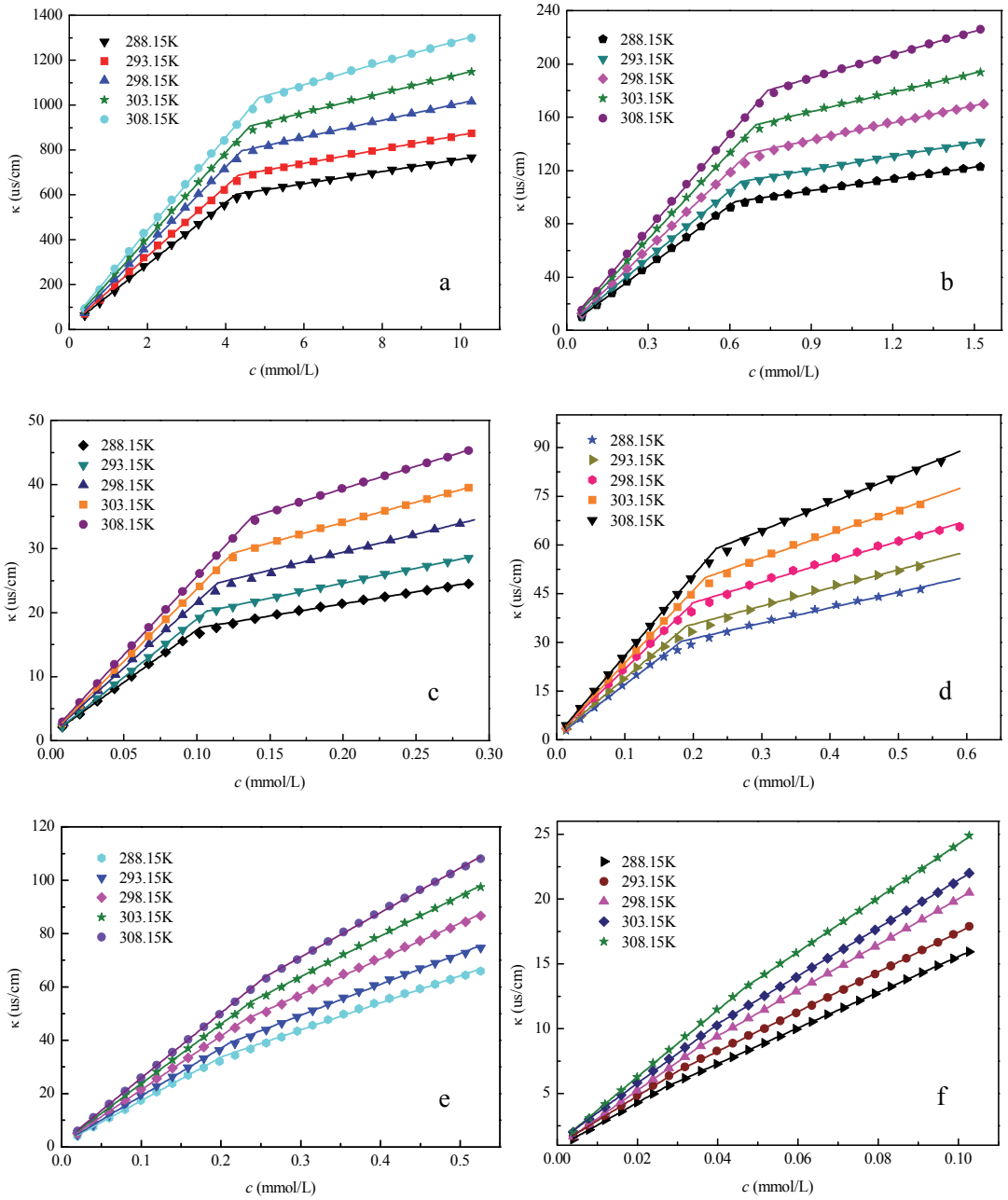


Figure S2. Conductivities of $C_{10}C_3C_{10}$PB (a), $C_{12}C_3C_{12}$PB (b), $C_{14}C_3C_{14}$PB (c), $C_{12}C_3C_{14}$PB (d), $C_{10}C_3C_{14}$PB (e), and $C_8C_3C_{16}$PB (f) at different temperature, respectively.

3. Concentration dependent ^{1}H NMR

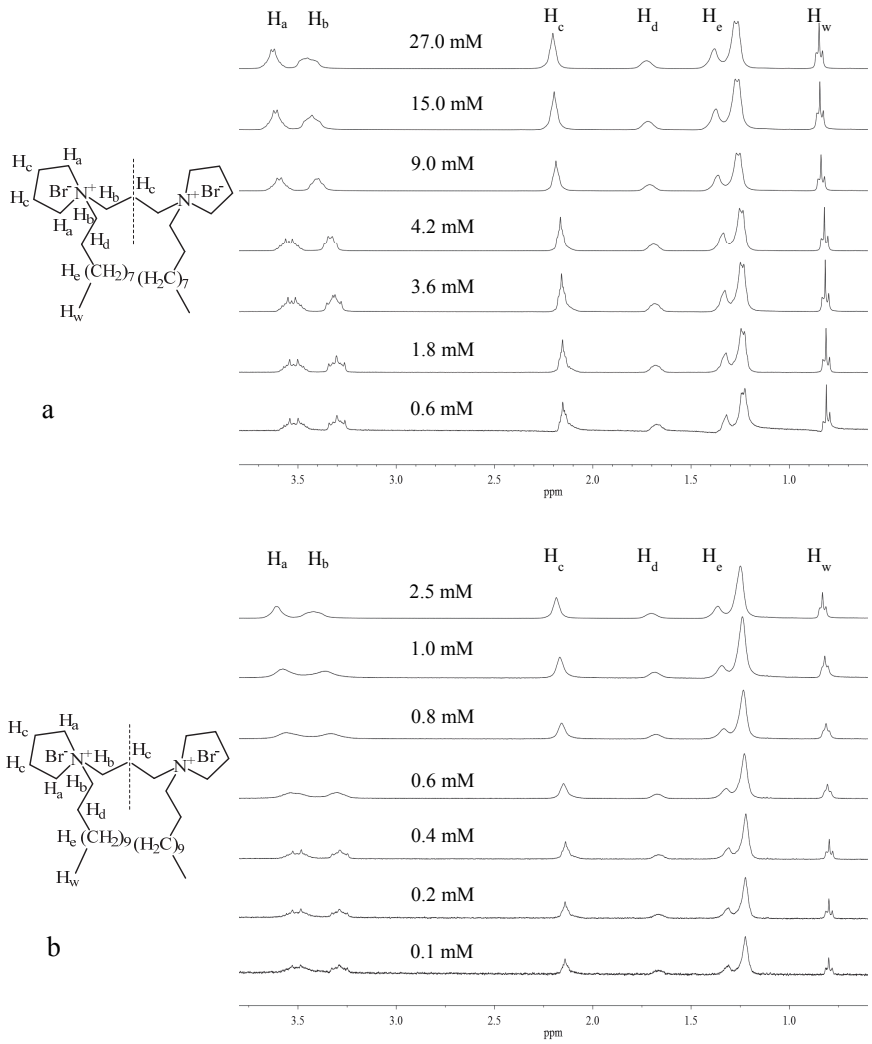


Figure S3. Concentration dependent ^{1}H NMR spectra and proton numbering of $C_{10}C_3C_{10}$PB (a) and $C_{12}C_3C_{12}$PB (b) in D_2O at 25 °C, respectively.

5. Concentration dependent chemical shifts

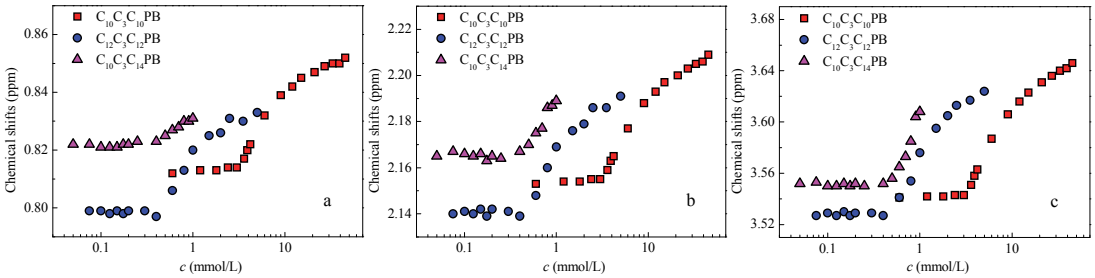


Figure S4. Variation of the chemical shifts (δ_{obs}) of the selected protons Hw (a), Hd (b) and Ha (c) versus the concentration (c) for $C_{10}C_3C_{10}$PB, $C_{12}C_3C_{12}$PB and $C_{10}C_3C_{14}$PB at 25 °C in D_2O, respectively.

6. 2D Noesy NMR spectra

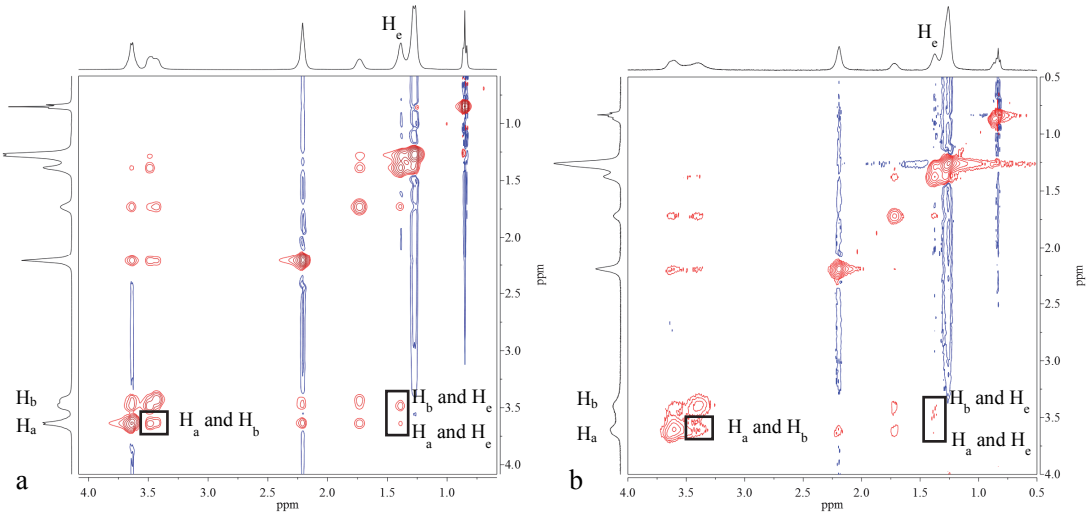


Figure S5. 2D Noesy NMR spectra of 45 mM $C_{10}C_3C_{10}$PB (a) and 1 mM $C_{10}C_3C_{14}$PB (b) in D_2O at 25 ^oC, respectively.

References

[1] B. Cai, X. F. Li, Y. Yang and J. F. Dong, *J. Colloid Interface Sci.,* 2012, **370**, 111.

[2] B. Cai, J. F. Dong, L. Cheng, Z. Jiang, Y. Yang and X. F. Li, *Soft Matter,* 2013, **9**, 7637.