Electronic Supplementary Information

Micellization and thermodynamics study of ester functionalized picoline-based ionic liquids surfactants in water

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Synthesis of ionic liquids (ILs)

General preparation of fatty acid 2-bromoethyl ester

Briefly, dodecanoic acid was mixed with 1 equivalent of 2-bromoethanol in a 100 mL three-necked flask while a trace amount H_2SO_4 as a catalyst was added, the system was reacted for 3 h at 60 ℃. After the reaction, the crude product was washed by 30 mL×3 H_2O and extracted by 50 mL×3 $CHCl_3$, then the organic phase was dry by Na_2SO_4. $CHCl_3$ was removed under a high vacuum. The pure dodecanoic acid 2-bromoethyl ester (C_{12}BrEE) was recrystallized in fresh methanol at least three times. The syntheses process of myristic acid 2-bromoethyl ester (C_{14}BrEE) and decanoic acid 2-bromoethyl ester (C_{10}BrEE) were identical. The myristic acid and decanoic acid were used to synthesize, respectively.

General procedure for the synthesis of [C_nEmpy][Br]

3-methylpyridinium was mixed with 1 equivalent of dodecyl 2-bromoethyl ester in 30 mL dry toluene in a 100 mL two-necked flask and refluxed for 6 h under nitrogen atmosphere. After the reaction, toluene was removed under a high vacuum and the pure [C_{12}Empy][Br] was recrystallized in fresh ethyl acetate at least three times.

C_{10}BrEE: yellow liquid. Yield: 93%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 4.421~4.285 (t, 2H), 3.539~3.509 (t, 2H), 2.378~2.316 (t, 2H), 1.668~1.633 (m, 2H), 1.280 (m,14H), 0.891~0.868 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 173.373, 63.595,61.997, 34.121, 31.870, 29.420, 24.913, 22.677, 14.110; FTIR (ν/cm^{-1}): 2959, 2916, 2844, 1738, 1695, 1455, 1394, 1175, 1099, 722.

C_{12}BrEE: yellow liquid. Yield: 92%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 4.400~4.369 (t, 2H), 3.525~3.494 (t, 2H), 2.365~2.328 (t, 2H), 1.656~1.621 (m, 2H), 1.262 (m, 18H), 0.898~0.864 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 179.601, 173.413, 63.608, 34.123, 31.921, 29.606, 24.916, 22.696, 14.116; FTIR (ν/cm^{-1}): 2920, 2852, 1738, 1710, 1462, 1376, 1153, 1107, 712.

C_{14}BrEE: white powder. Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 4.402~4.371 (t, 2H), 3.526~3.496 (t, 2H), 2.367~2.329 (t, 2H), 1.658~1.605 (m, 2H), 1.262 (m, 22H), 0.901~0.866 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 179.662, 173.412, 63.609, 34.134, 31.939, 29.658, 24.918, 22.706, 14.124; FTIR (ν/cm^{-1}): 2956, 2912, 2848, 1735, 1692, 1466, 1383, 1171, 1092, 719.

[C_{10}Empy][Br]: pink powder. Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 9.509 (s, H), 9.347 (d, 1H), 8.331 (d, 1H), 8.038 (t, 1H), 5.371 (s, 2H), 4.639 (s, 2H), 2.642 (s, 3H), 2.278~2.241 (m, 2H), 1.6485 (m, 2H), 1.213 (m, 14H), 0.863 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 172.910, 146.323, 145.195, 142.907, 139.510, 127.573, 63.234, 60.205, 33.888, 31.826, 29.383, 29.226, 29.632, 29.035, 24.703, 22.637, 18.731, 14.096; FTIR (v/cm^{-1}): 3017, 2992, 2923, 2841, 1735, 1634, 1502, 1462, 1390, 1146, 1085, 719.

[C_{12}Empy][Br]: white powder. Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 9.498 (s, H), 9.326 (d, 1H), 8.305 (d, 1H), 8.018 (t, 1H), 5.339~5.319 (t, 2H), 4.614~4.590 (t, 2H), 2.619 (s, 3H), 2.248~2.210 (t, 2H), 1.468~1.435 (t, 2H), 1.179 (m, 18H), 0.839~0.807 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 172.894, 146.347, 146.299, s145.189, 142.917, 138.481, 127.568, 62.698, 60.169, 33.871, 31.860, 29.563, 29.422, 29.288, 29.227, 29.028, 24.686, 22.640, 18.704, 14.086; FTIR (v/cm^{-1}): 3017, 2992, 2920, 2844, 1728, 1638, 1509, 1466, 1387, 1146, 1082, 726.

[C_{14}Empy][Br]: white powder. Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 9.476 (s, H), 9.317 (d, 1H), 8.300 (d, 1H), 8.017 (t, 1H), 5.343~5.322 (t, 2H), 4.618~4.594 (t, 2H), 2.615 (s, 3H), 2.255~2.210 (t, 2H), 1.478~1.445 (t, 2H), 1.212 (m, 22H), 0.851~0.817 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 172.913, 146.263, 145.266, 145.202, 142.938, 139.473, 127.553, 62.698, 60.221, 33.879, 31.890, 29.655, 29.622, 29.586, 29.447, 29.247, 29.134, 29.046, 24.698, 22.659, 18.708, 14.066; FTIR (v/cm^{-1}): 3013, 2992, 2912, 2844, 1735, 1634, 1509, 1469, 1387, 1146, 1017, 719.

The purity of the synthesized ionic liquids was estimated by ^{1}H NMR, and the purity of [C_nEmpy][Br] (n=10, 12, 14) were 98.6%, 99.3% and 99.4%, respectively.

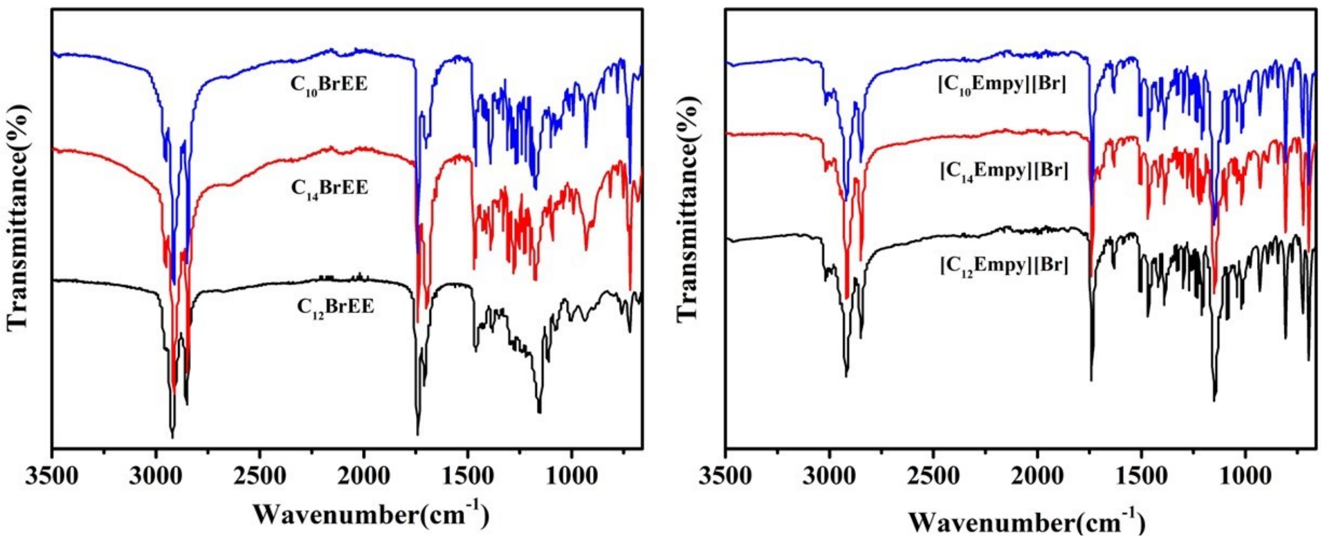

Fig. S1. FTIR spectrum of synthesized C_nBrEE and [C_nEmpy][Br]

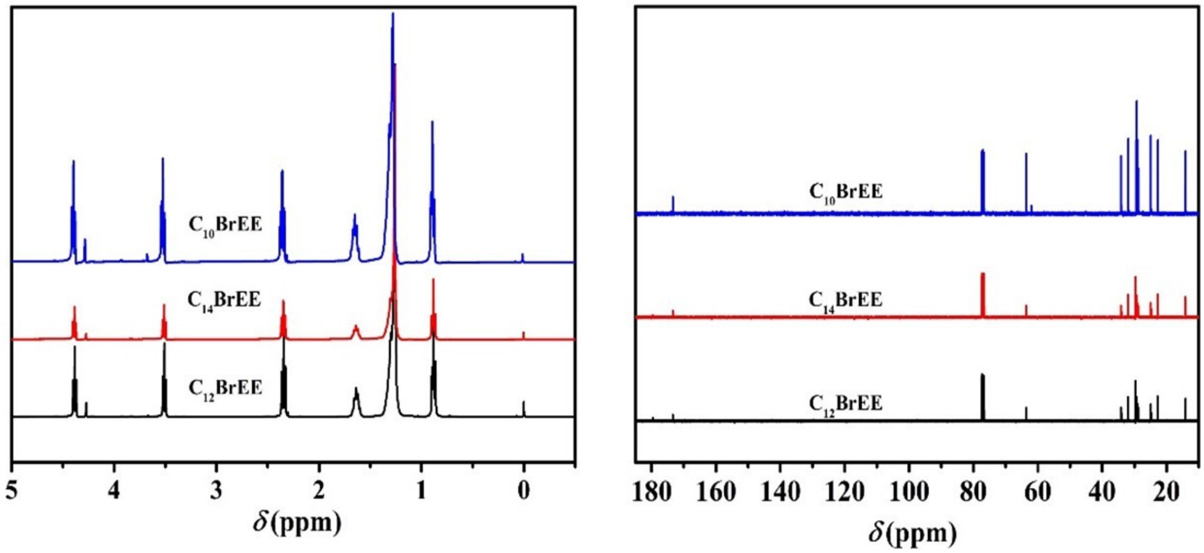

Fig. S2. (^{1}H, ^{13}C) NMR spectrum of synthesized C_nBrEE

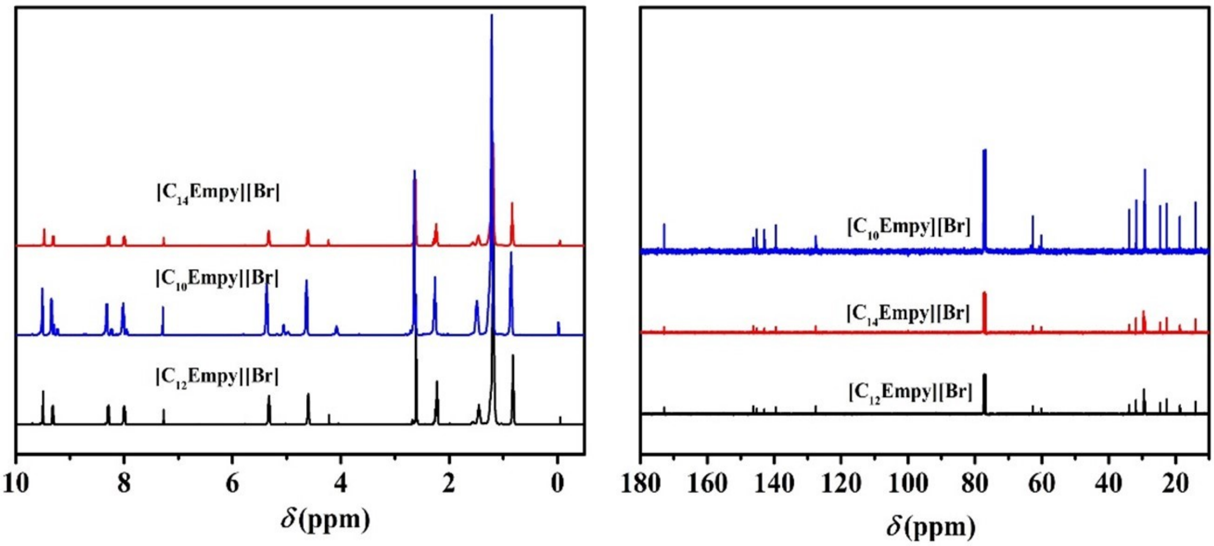

Fig. S3. (^{1}H, ^{13}C) NMR spectrum of synthesized [C_nEmpy][Br]

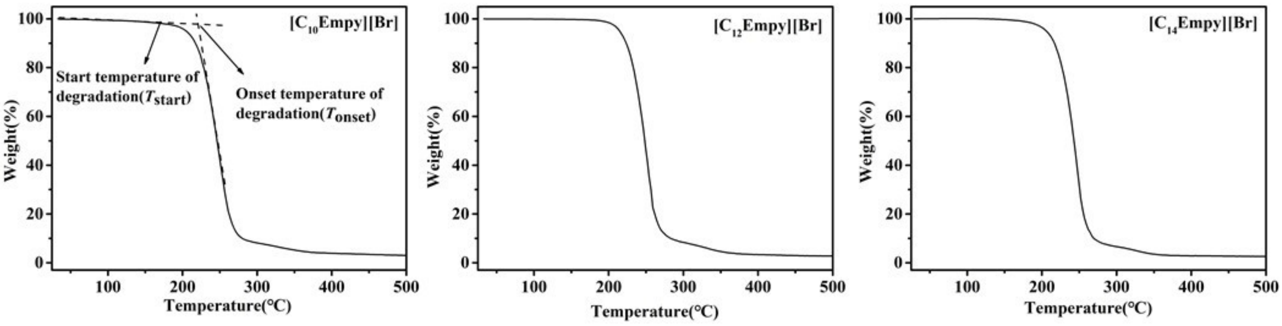

Fig. S4. TGA curve of synthesized [C_nEmpy][Br]

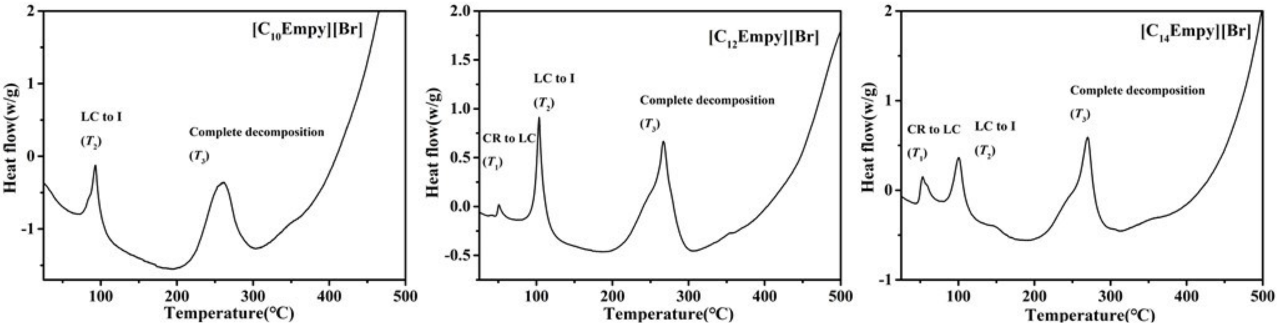

Fig. S5. DSC curve of synthesized [C_nEmpy][Br]. The temperature at which the ionic liquids transform from CR phase to LC phase is the melting point of the ionic liquids (ie T_1), and the temperature at which the ionic liquids transform from LC phase to I phase is the thermal transition temperatures of the ionic liquids (ie T_2).

Table S1 Coefficients of polynomials CMC=A+ BT + CT^2; the temperature T^*(CMC), at the minimum critical micelle concentration, CMC*

ILs	A	B	C	CMC*	T^*
[C_{10}Empy][Br]	418.03088	-2.694	0.00458	21.84	294.11
[C_{12}Empy][Br]	141.446	-0.9305	0.0016	6.16	290.80
[C_{14}Empy][Br]	72.6781	-0.4890	8.4697×10^{-4}	2.10	288.68

Units: T(K); B(K^{-1}); C(K^{-2}); T*(K); CMC*(mmol·L^{-1})

Table S2 Coefficients of polynomials Log X_{CMC}=A+ BT + CT^2; T_0 at ΔH_{mic}^{θ}=0; together with the "chemical part" of the micellization process, ΔH_c^{θ}, compensation temperature, T_c and standard heat capacity change upon micelle formation, $\Delta C_{p,mic}^{\theta}$, for the investigated systems.

ILs	A	B	C	T_0	$\Delta C_{p,mic}^{\theta}$	ΔH_c^{θ}	T_c
[C_{10}Empy][Br]	5.64556	-0.04967	8.4507×10^{-5}	292.84	-466.44	-29.13	271.28
[C_{12}Empy][Br]	6.96792	-0.06314	1.0835×10^{-4}	290.67	-638.47	-36.76	287.80
[C_{14}Empy][Br]	10.2092	-0.08915	1.5419×10^{-4}	288.59	-926.00	-41.16	288.16

Units: T(K); B(K^{-1}); C(K^{-2}); T_0, T_c(K); ΔH_c^{θ}, kJ mol^{-1}, $\Delta C_{p,mic}^{\theta}$ (J·K^{-1}·mol^{-1}).