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Effect of Alkyl Chain Functionalization of Ionic Liquid Surfactants on Complexation and Self-Assembling Behavior of Polyampholyte Gelatin in Aqueous Medium

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Supporting Information

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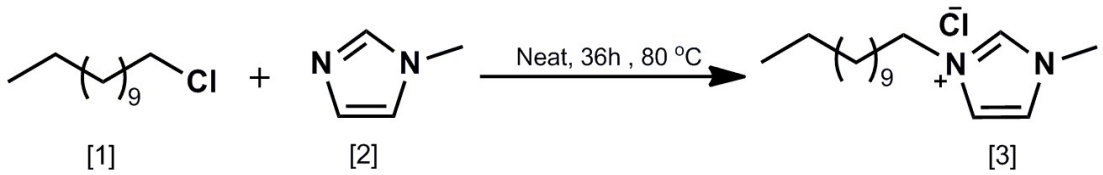
Annexure S1: Synthetic procedure for the preparation of ionic liquid surfactants (ILSs)

Synthesis of [C_{12}mim][Cl]: The synthetic procedure followed for the synthesis of [C_{12}mim][Cl] is provided schematically in Scheme S1. Dodecyl chloride (1; 13.71g, 66.9 mmol) and 1-methylimidazole (2; 5 g, 60.9 mmol) were mixed and stirred at 80 °C for 36 h. The reaction mixture was then cooled to 20 °C, after that it was washed thrice with 50 ml diethyl ether and only once with 50 hexane. The resulting product was purified by recrystallization from acetone at least three times and then dried under vacuum for 1 day.



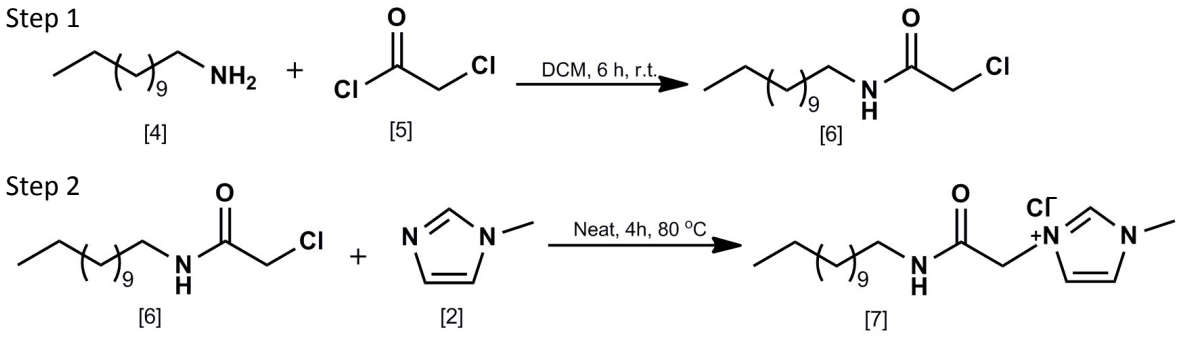
[1] [2] [3]

Scheme S1: Reaction scheme for the synthesis of ILS-1, [C_{12}mim][Cl].

^{1}H NMR (500 MHz, $CdCl_3$, δ-ppm) 0.879 (t, 3H, CH_3), 1.248 (br s, 18H, (-CH_2-)$_9$), 1.905 (q, 2H, -N$^+$-CH_2- CH_2-), 4.131 (s, 3H, -N-CH_3), 4.316 (t, 3H, -N$^+$-CH_2-CH_2-), 7.360 (s, 1H, -N-C*H*-CH-N$^+$-), 7.528 (s, 1H, -N-CH-C*H*-N$^+$-), 10.572 (s, 1H, -N-C*H*-N$^+$-). ESI-HRMS positive ions m/z (for $C_{16}H_{31}N_2^+$): 251.2624, 252.2652.

Synthesis of [C_{12}Amim][Cl]: The synthetic procedure followed for the synthesis of [C_{12}Amim][Cl] is provided schematically in Scheme S2. Solution of 1-aminododecane (4; 11.98 g, 70 mmol) in dichloromethane (50 mL) was added drop wise to a stirred solution of chloro acetyl chloride (5; 8.69 g, 77 mmol) in dichloromethane (50 mL) cooled at 4°C within 30-40 minutes. After 1 hour, the ice bath was removed and the reaction mixture was stirred for 4-5 h at room temperature. The pH of the reaction mixture was raised to 9 by adding 6 M NaOH solution. Using separating funnel, the dichloromethane layer was separated and the solvent was removed under reduced pressure in a rotary flash evaporator at 40°C. After that, the reaction mixture was washed with 100 ml of warm aqueous ethanol. The lower layer consisting of 2-chloro-N-dodecylacetamide (6) was separated using separating funnel. The resulting product was dried using vacuum rotary flash evaporator at 80°C for 2 hours. N-Methyl imidazole (2; 1.23 g, 15 mmol) and the above synthesized intermediates 2-chloro-N-dodecylacetamides (6; 3.57 g, 13.6 mmol) were mixed and stirred at 80 °C for 4 hours. Then

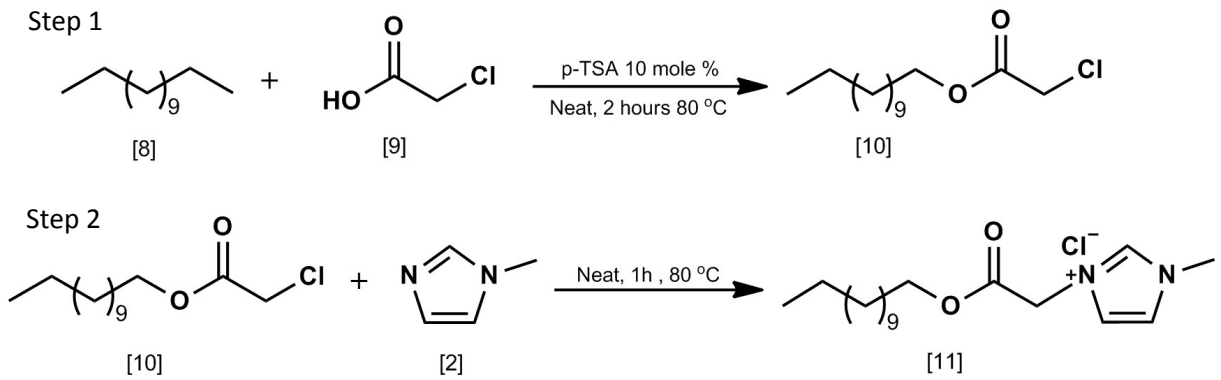
the reaction mixture was cooled to 20 °C and was washed thrice with 50 ml of diethyl ether. Further the product was re-crystallized using ethyl acetate.



Scheme S2: Reaction scheme for the preparation of amide functionalized ILS-2, [C_{12}Amim][Cl].

^{1}H NMR (500 MHz, $CdCl_3$, δ-ppm) 0.878 (t, 3H, -CH_2-CH_3), 1.243 (br s, 18H, (-CH_2-)$_9$), 1.553 (q, 2H, (-CONH-CH_2- CH_2-)), 3.202 (t, 3H, -CONH-CH_2-CH_2-), 4.017 (s, 3H, -N-CH_3), 5.292 (s, 2H, -N^+-CH_2-CONH-), 7.237 (s, 1H, -N-C*H*-CH-N^+), 7.640 (s, 1H, -N-CH-C*H*-N^+), 8.934 (s, 1H, (-CON*H*-CH_2-), 9.806 (s, 1H, -N-C*H*-N^+-). ESI-HRMS positive ions m/z (for $C_{18}H_{34}N_3O^+$): 308.2847, 309.2774.

Synthesis of [C_{12}Emim][Cl]: The synthetic procedure followed for the synthesis of [C_{12}Amim][Cl] is provided schematically in Scheme S3. To the mixture of dodecan-1-ol (8; 5.17 g, 30 mmol) and chloroacetic acid (9; 2.83 g, 30 mmol), a catalytic amount (10 mol%) of p-toluene sulphonic acid (5; 380.43 mg, 2 mmol) was added and whole reaction mixture under solvent-free condition was stirred for 2 h at 80 °C. Thin layer chromatography in 2% ethyl acetate-hexane was used to monitor the progress of reaction. After cooling the reaction mixture to room temperature, it was dissolved in 100 ml of chloroform and washed twice with 100 ml of water. The chloroform layer was separated using separating funnel and solvent was removed under reduced pressure in a rotary flash evaporator at 40 °C followed by washing with 100 ml of warm aqueous methanol (92:8, methanol/water). The lower layer containing dodecyl- 2-haloacetate (10) was separated and dried using vacuum rotary flash evaporator at 80 °C for 2 hours. The resulting intermediate dodecyl-2-chloroacetate (10; 3.56 g, 13.6 mmol) was allowed to react with N-methylimidazole (2; 1.23 g, 15 mmol) at 80 °C for 3-4 hour. After cooling to 20 °C, the product was washed thrice with 50 ml of diethyl ether and then cold precipitated in 50 ml of acetone.



Scheme S3: Reaction scheme for the preparation of ester functionalized ILS-3, $[C_{12}Emim][Cl]$.

^{1}H NMR (500 MHz, $CdCl_3$, δ-ppm) 0.881 (t, 3H, C*H*$_3$), 1.262 (br s, 18H, (-C*H*$_2$-)$_9$), 1.657 (q, 2H, -COO-CH$_2$- C*H*$_2$-), 4.073 (s, 3H, -N-C*H*$_3$), 4.117 (t, 3H, -COO-C*H*$_2$-CH$_2$-), 5.460 (s, 2H, -N$^+$-C*H*$_2$-COO-), 7.532 (s, 1H, -N-C*H*-CH-N$^+$-), 7.579 (s, 1H, -N-CH-C*H*-N$^+$-), 10.128 (s, 1H, -N-C*H*-N$^+$-). ESI-HRMS positive ions m/z (for $C_{18}H_{33}N_2O_2^+$): 309.2679, 310.2712.

Table S1: The names of the chemicals used for the synthesis of ILSs as well as those used for other investigations along with their respective purity.

S.No.	Name of Chemical	Purity
1.	Chloroacetyl chloride	Sigma (98%)
2.	1-aminododecane	Sigma (≥99%)
3.	N-methyl imidazole	Sigma (≥99%)
4.	Dodecan-1-ol	Sigma (98%)
5.	1-chlorododecane	Sigma (≥97%)
6.	Pyrene	Sigma (≥99%)
7.	p-toluenesulfonic acid	Sigma (≥98.5%)
8.	Chloroacetic acid	Sigma (≥98%)
9.	Dihydrogen sodium phosphate, Disodium hydrogen phosphate and Sodium hydroxide	AR grade, Qualigens, India.
10.	Dichloromethane, acetone, absolute ethanol, methanol, chloroform, hexane and diethyl ether, ethyl acetate.	AR grade, SD Fine-Chem Ltd., Mumbai, India.

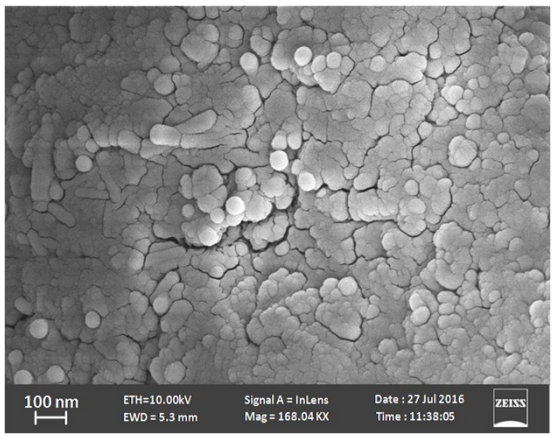


Figure S1: Scanning Electron micrograph (SEM) of gelatin in buffer solution as a control experiment.

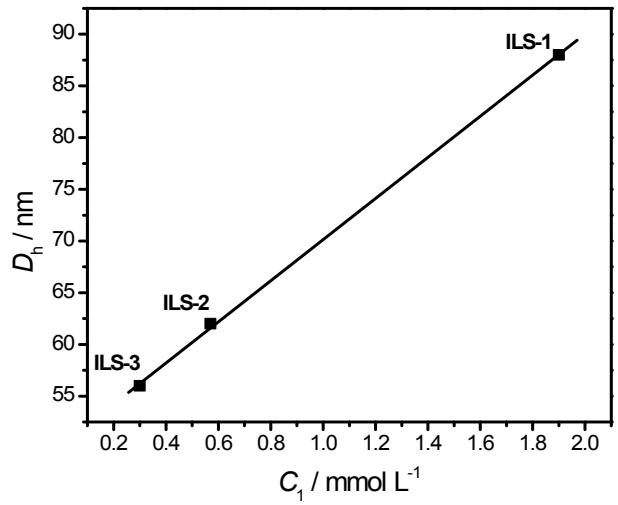


Figure S2: Variation of hydrodynamic diameter (D_h) in G-ILS systems for different ILSs as a function of observed C_1 obtained from DLS measurements.

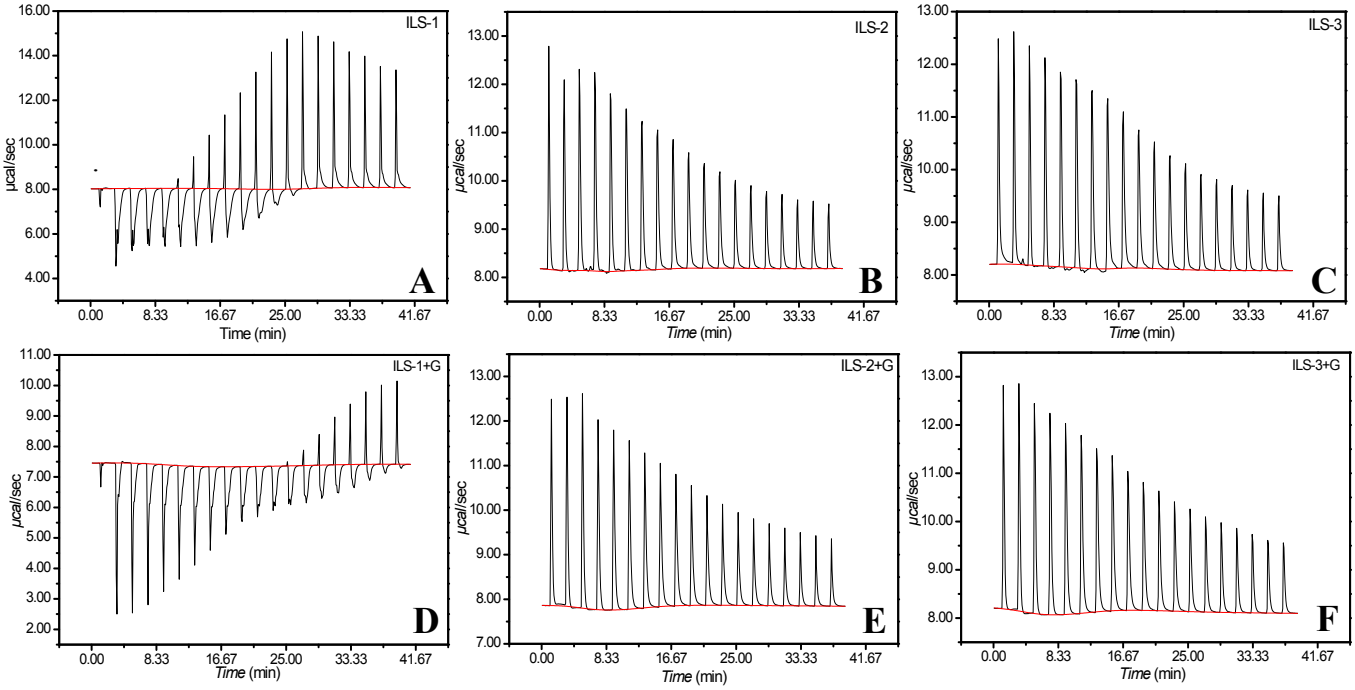


Figure S3(A-F): Differential power (dP) profiles in different buffer solutions of ILSs in the absence (A-C) and presence (D-F) of gelatine at 298.15 K.

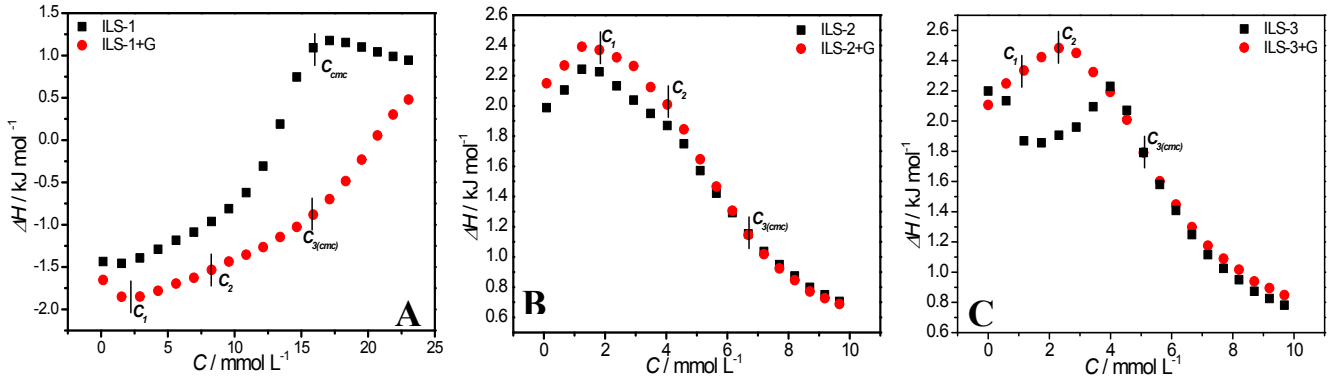


Figure S4(A-C): The enthalpogram of ILSs as the function of concentration in aqueous buffer solutions with and without gelatin.