

## **Effect of Cationic Head Group on Micellization Behavior of New Amide Functionalized Surface Active Ionic Liquids**

Raman Kamboj,<sup>‡</sup> Pankaj Bharmoria,<sup>†</sup> Vinay Chauhan,<sup>‡</sup> Gurbir Singh,<sup>‡</sup> Arvind Kumar,<sup>†</sup>  
Sukhprit Singh,<sup>‡,\*</sup> Tejwant Singh Kang<sup>‡,\*</sup>

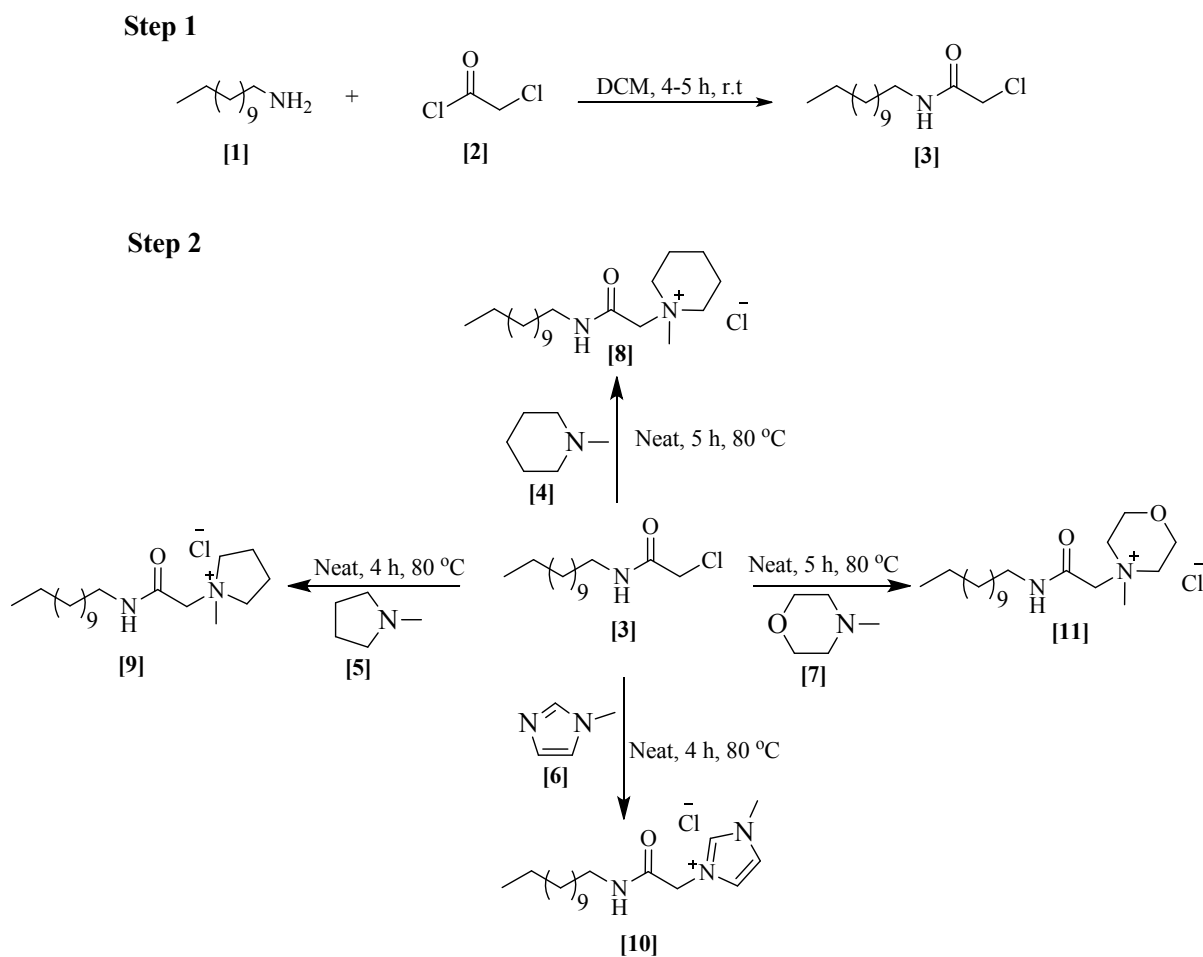
*<sup>‡</sup>Department of Chemistry, UGC-Centre for Advanced Studies-I, Guru Nanak Dev University,  
Amritsar-143005, India*

*<sup>†</sup>Academy of Scientific and Innovative Research (AcSIR), <sup>¶</sup>Salts and Marine Chemicals  
Division, CSIR-Central Salt and Marine Chemicals Research Institute, Council of Scientific  
& Industrial Research (CSIR), G. B. Marg, Bhavnagar-364002, Gujarat, India*

### **Supporting Information**

## Annexure S1: Synthesis of Amide Functionalized SAILs:

The 2-chloro-*N*-dodecylacetamides (**3**) were synthesized according to the reported procedure with some modifications. 1-aminododecane (**1**; 75 mmol, 13.86 g) in dichloromethane (50 mL) was added dropwise to a stirred solution of chloroacetyl chloride (**2**; 82.5 mmol, 6.54 g) in dichloromethane (50 mL) cooled in an ice-water bath. After 30 min the ice bath was removed, and the reaction mixture was stirred for 4-5 h at room temperature and then neutralized to a pH of 9 with NaOH solution (6 M).



Scheme - S1

The dichloromethane layer was separated from separating funnel and was removed from the crude reaction mixture under reduced pressure in a rotary flash evaporator at 40°C. The crude reaction mixture was then washed with 100 ml of warm aqueous ethanol. The lower layer

consisting of 2-chloro-*N*-dodecylacetamides (**3**) was allowed to separate in separating funnel. It was then separated and dried using vacuum rotary flash evaporator at 80°C for 30 minutes.

The resulting intermediates 2-chloro-*N*-dodecylacetamides (**3**; 10 mmol, 2.61 g) was then reacted with *N*-Methyl piperidine (**4**; 11 mmol, 1.33 g), *N*-Methyl pyrrolidine (**5**; 11 mmol, 1.14 g), *N*-Methyl imidazole (**6**; 11 mmol, 0.90 g) and *N*-methyl morpholine (**7**; 11 mmol, 1.11 g) at 80 °C for 4-5 hour (**Scheme-S1**). The resulting crude mixture was cooled to 20 °C. The product was washed thrice with 50 ml of diethyl ether and then recrystallized with 30 ml of ethyl acetate to get pure amide functionalized surface active ionic liquids (SAILs), with different cationic head group's (**8-11**). The structures of all of these products were confirmed by NMR, and mass spectrometry. Mass spectra were recorded on Waters Q-ToF micromass equipment using ESI as the ion source. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either an AL-300 (JEOL, Japan) FT-NMR (300 MHz) system or a Bruker Avance II (Switzerland) FT-NMR (400 MHz) system as a solution in CDCl<sub>3</sub> using tetramethylsilane (TMS) as the internal standard. The NMR and Mass data of the synthesized SAILs is provided in Annexure I (supporting information).

#### **8. 1-(2-(dodecylamino)-2-oxoethyl)-1-methylpiperidin-1-ium chloride [C<sub>12</sub>APip][Cl]:**

White powder, Yield 74%; 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS) δ ppm: 0.82-0.85 (t, 3H, terminal CH<sub>3</sub>), 1.20-1.25 (br s, 18H, (-CH<sub>2</sub>)<sub>9</sub>), 1.50-1.53 (m, 2H, -NHCH<sub>2</sub>CH<sub>2</sub>-), 1.86 (m, 2H, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.86-1.96 (m, 4H, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.16-3.19 (m, 2H, -CH<sub>2</sub>NHCO), 3.39 (s, 3H, -N<sup>+</sup>CH<sub>3</sub>), 3.53-3.55 (m, 2H, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.87-3.89 (m, 2H, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.54 (s, 2H, -N<sup>+</sup>CH<sub>2</sub>CO-), 9.21 (br s, 1H, -NH-). 75 MHz <sup>13</sup>C/DEPT NMR (CDCl<sub>3</sub>) δ ppm: 14.07 (-ve, terminal -CH<sub>3</sub>), 20.15-31.86 (+ve, -CH<sub>2</sub> chain and -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 39.80 (+ve, -CH<sub>2</sub>NHCO-), 49.15 (-ve, -N<sup>+</sup>CH<sub>3</sub>), 55.05 (+ve, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 62.47 (+ve, -N<sup>+</sup>CH<sub>2</sub>CO-), 162.33 (-CH<sub>2</sub>CONH-). MS positive ions m/z

(for  $C_{20}H_{41}N_2O^+$ ): 325.3239 (M-Cl)<sup>+</sup>. Elemental analysis: C (73.6%); H (12.7%); N (8.7%); O (5.0%).

**9. 1-(2-(dodecylamino)-2-oxoethyl)-1-methylpyrrolidin-1-ium chloride [C<sub>12</sub>APyrr][Cl]:**

White powder, Yield 76%; 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS) δ ppm: 0.89-0.93 (t, 3H, terminal CH<sub>3</sub>), 1.28 (br s, 18H, (-CH<sub>2</sub>)<sub>9</sub>), 1.61 (m, 2H, -NHCH<sub>2</sub>CH<sub>2</sub>-), 2.24-2.40 (m, 4H, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>-), 3.29 (m, 2H, -CH<sub>2</sub>NHCO), 3.39 (s, 3H, -N<sup>+</sup>CH<sub>3</sub>), 3.77-4.04 (m, 4H, -N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>-), 4.57 (s, 2H, -N<sup>+</sup>CH<sub>2</sub>CO-), 9.25 (br s, 1H, -NH-). 75 MHz <sup>13</sup>C/DEPT NMR (CDCl<sub>3</sub>) δ ppm: 14.02 (-ve, terminal -CH<sub>3</sub>), 21.90-31.72 (+ve, -CH<sub>2</sub> chain), 36.53 (+ve, -CH<sub>2</sub>NHCO-), 49.74 (-ve, -N<sup>+</sup>CH<sub>3</sub>), 60.66-60.91 (+ve, ring carbons), 63.91 (+ve, -N<sup>+</sup>CH<sub>2</sub>CO-), 123.4 (+ve, -NCHCHN<sup>+</sup>-), 137.2 (+ve, -NCHN<sup>+</sup>-), 162.40 (-CH<sub>2</sub>CONH-). MS positive ions m/z (for C<sub>19</sub>H<sub>39</sub>N<sub>2</sub>O<sup>+</sup>): 311.3070 (M-Cl)<sup>+</sup>. Elemental analysis: C (73.2%); H (12.7%); N (9.0%); O (5.1%).

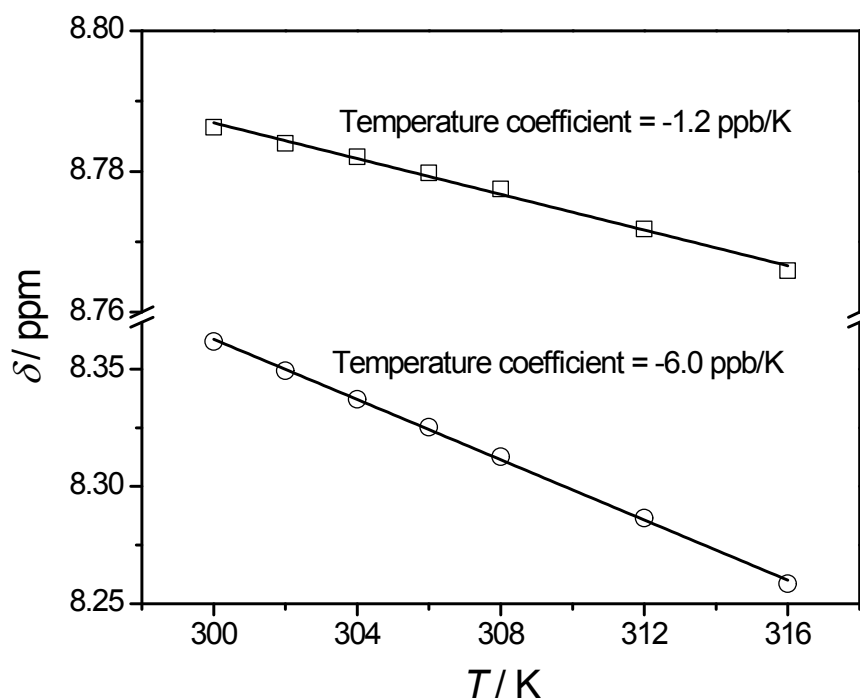
**10. 3-(2-(dodecylamino)-2-oxoethyl)-1-methyl-1H-imidazol-3-ium chloride [C<sub>12</sub>AMim][Cl]:**

White powder; Yield 75%; 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS): δ (ppm) 0.88 (t, 3H, terminal CH<sub>3</sub>), 1.24 (br. s, 18H, (-CH<sub>2</sub>)<sub>9</sub>), 1.56 (m, 2H, -NHCH<sub>2</sub>CH<sub>2</sub>-), 3.22 (m, 2H, -CH<sub>2</sub>NHCO), 4.00 (s, 3H, -N<sup>+</sup>CH<sub>3</sub>), 5.31 (s, 2H, -N<sup>+</sup>CH<sub>2</sub>CO-), 7.15 (s, 1H, -NCHCHN<sup>+</sup>), 7.65 (s, 1H, -NCHCHN<sup>+</sup>), 8.96 (br s, 1H, -NH-), 9.97 (s, 1H, -NCHN<sup>+</sup>). 75 MHz <sup>13</sup>C/DEPT-135 NMR (CDCl<sub>3</sub>): δ (ppm) 14.09 (+ve, terminal CH<sub>3</sub>), 22.64-31.86 (-ve, CH<sub>2</sub> chain), 36.53 (-ve, -N<sup>+</sup>CH<sub>3</sub>), 40.34 (+ve, -CH<sub>2</sub>NHCO-), 62.37 (+ve, -N<sup>+</sup>CH<sub>2</sub>CO-), 127.72 (+ve, -NCHCHN<sup>+</sup>-), 145.6 (+ve, -NCHN<sup>+</sup>-), 162.48 (-CH<sub>2</sub>CONH-). MS positive ions m/z (for C<sub>18</sub>H<sub>34</sub>N<sub>3</sub>O<sup>+</sup>): 308.2696 (M-Cl)<sup>+</sup>. Elemental analysis: C (69.9%); H (11.1%); N (13.8%); O (5.2%).

**11. 4-(2-(dodecylamino)-2-oxoethyl)-4-methylmorpholin-4-ium chloride [C<sub>12</sub>AMorph][Cl]:**

White powder, Yield 77%; 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS) δ ppm: 0.88 (t, 3H,

terminal  $CH_3$ ), 1.25 (br s, 18H,  $(-CH_2-)_9$ ), 1.58 (m, 2H,  $-NHCH_2CH_2-$ ), 3.24 (m, 2H,  $-CH_2NHCO$ ), 3.58 (s, 3H,  $-N^+CH_3$ ), 4.03-4.12 (m, 8H, ring  $CH_2$ ), 4.83 (s, 2H,  $-N^+CH_2CO-$ ), 9.09 (br s, 1H,  $-NH-$ ). 75 MHz  $^{13}C/DEPT$  NMR ( $CDCl_3$ )  $\delta$  ppm: 14.10 ( $-ve$ , terminal  $-CH_3$ ), 22.68-31.92 ( $+ve$ ,  $-CH_2$  chain), 39.90 ( $+ve$ ,  $-CH_2NHCO-$ ), 53.48 ( $-ve$ ,  $-N^+CH_3$ ), 60.66-60.91 ( $+ve$ , ring carbons), 63.91 ( $+ve$ ,  $-N^+CH_2CO-$ ), 162.40 ( $-CH_2CONH-$ ). MS positive ions  $m/z$  (for  $C_{19}H_{39}N_2O_2^+$ ): 327.2989 ( $M-Cl$ ) $^+$ . Elemental analysis: C (69.8%); H (11.9%); N (8.4%); O (9.9%).



**Figure S1.** Variation of chemical shift ( $\delta$ ) for ( $\square$ ) amide proton; and ( $\circ$ ) most acidic proton of imidazolium ring placed between two N-atoms in micellar solutions of  $[C_{12}Amim][Cl]$  as a function of temperature. The concentration of aqueous solution of  $[C_{12}Amim][Cl]$  was  $10 \text{ mmol L}^{-1}$ .

**Table S1.** Comparison of temperature corresponding to onset of thermal degradation ( $T_{\text{onset}}$ ) of various functionalized and non-functionalized ILs.

<i>Functionalization</i>	<i>Abbreviation of IL</i>	$T_{\text{onset}}$ ( $^{\circ}\text{C}$ )
Amide functionalized Morpholinium based	[C <sub>12</sub> APip][Cl]	196
	[C <sub>12</sub> APyrr][Cl]	211
	[C <sub>12</sub> Amim][Cl]	218
	[C <sub>12</sub> AMorph][Cl]	182
Ester functionalized imidazolium based	[C <sub>8</sub> Emim][Br]	212 <sup>1</sup>
	[C <sub>12</sub> Emim][Br]	220 <sup>1</sup>
Ester functionalized pyridinium based	[C <sub>8</sub> Pyrr][Br]	158 <sup>1</sup>
	[C <sub>12</sub> Pyrr][Br]	160 <sup>1</sup>
Non-functionalized imidazolium based	[C <sub>12</sub> mim][Br]	282 <sup>2</sup>
	[C <sub>12</sub> Pyrr][Br]	506 <sup>3</sup>

**Table S2.** Hydrodynamic diameter ( $D_h$ ), polydispersity index (PDI), and size from AFM measurements of aggregates of SAILs at 298.15 K.

SAIL	Size / nm				
	DLS		PDI	AFM	
	Micelles	Agg.		Micelles	Agg.
[C <sub>12</sub> APip][Cl]	1.9	60	0.37	10-15	70-130
[C <sub>12</sub> Amim][Cl]	2.7	90	0.33	10-20	60-150
[C <sub>12</sub> APyrr][Cl]	4.4	64	0.29	15-30	80-140
[C <sub>12</sub> AMorph][Cl]	5.5	205	0.30	20-35	80-180

PDI was determined using the software (Zetasizer software 7.03) provided with the dynamic light scattering measurement apparatus. Agg. represents the agglomerates.

## References:

1. Garcia, M. T.; Ribosa, I.; Perez, L.; Manresa, A.; Comelles, F. *Langmuir* **2013**, *29*, 2536–2545.
2. Arellano, I. H. J.; Guarino, J. G.; Paredes, F. U.; Arco, S. D. *J. Therm. Anal. Calorim.*, **2011**, *103*, 725–730.
3. Youns, N. M.; Mutalib, M. I. A.; Man, Z.; Bustam, M. A.; Murugesan, T. *J. Chem. Thermodyn.*, **2010**, *42*, 491–495.