Electronic Supporting Information

Effect of Amide Bonds on the Self-assembly of Gemini Surfactants

Jiaul Hoque[a], Spandhana Gonuguntla[a], Venkateswarlu Yarlagadda[a], Vinod K. Aswal[b] and Jayanta Haldar[a]*

[a]*Chemical Biology and Medicinal Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bengaluru 560064, India.*

[b]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India.*

***Corresponding Author**

Telephone: +91-80-2208-2565; Fax: +91-80-2208-2627

E-mail: jayanta@jncasr.ac.in

1. Characterization of the surfactants used in the study.

1a: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.883 (t, terminal –*CH_3*, 6H), 1.289 (m, –CH_3*$(CH_2)_9$*–, 36H), 1.456 (–$(Me)_2^+NCH_2CH_2$*$(CH_2)_4$*–, 8H), 1.614 (m, –$CH_3(CH_2)_9$*CH_2*–, 4H), 1.935 (m, $Me_2N^+CH_2$*CH_2*–, 4H), 3.514 (s, –*CH_3*N^+–, 12H), 3.615 (m, –$CH_3(CH_2)_9CH_2$*CH_2*–, 4H), 3.778 (m, –$(Me)_2^+N$*CH_2*–, 4H); HRMS: m/z 269.5086 (calculated), 269.3942 (found), $[M–2Br]^{2+}$.

1b: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.859 (t, terminal –*CH_3*, 6H), 1.279 (m, –CH_3*$(CH_2)_9$*–, 36H), 1.764 (m, –$CH_3(CH_2)_9$*CH_2*–, 4H), 3.437 (s, –*CH_3*N^+–, 12H), 3.445 (m, – $(Me)_2^+N$ *CH_2*–, 4H), 3.619, (m, –CONH*CH_2*–, 4H), 4.653 (m, – $(Me)_2^+N$ *CH_2*CO–, 4H), 8.887 (br m, amide –*NH*, 2H); HRMS: m/z 288.2884 (calculated), 288.1076 (found), $[M–2Br]^{2+}$.

2b: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.872 (t, terminal –*CH_3*, 6H), 1.234 (m, –CH_3*$(CH_2)_9$*–, 36H), 1.456 (– $(Me)_2^+NCH_2CH_2$ *$(CH_2)_4$*–, 8H), 1.540 (m, –$CH_3(CH_2)_9$*CH_2*–, 4H), 1.932 (m, $Me_2N^+CH_2$*CH_2*–, 4H) 3.221 (m, –CONH*CH_2*–, 4H), 3.429 (s, –*CH_3*N^+–, 12H), 3.731 (m, – $(Me)_2^+N$ *CH_2*–, 4H), 4.521 (s, –NHCO*CH_2*–, 4H), 8.735 (br m, amide –*NH*, 2H); HRMS: m/z 340.5886 (calculated), 340.3446 (found), $[M–2Br]^{2+}$.

3: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.872 (t, terminal –*CH_3*, 6H), 1.293 (m, –CH_3*$(CH_2)_{13}$*–, 52H), 1.778 (m, –$CH_3(CH_2)_{13}$*CH_2*–, 4H), 3.410 (s, –*CH_3*N^+–, 12H), 3.456 (m, – $(Me)_2^+N$ *CH_2*–, 4H), 3.611, (m, –CONH*CH_2*–, 4H), 4.671 (m, – $(Me)_2^+N$ *CH_2*CO–, 4H), 8.943 (br m, amide –*NH*, 2H); HRMS: m/z 326.5596 (calculated), 326.3527 (found), $[M–2Br]^{2+}$.

4a: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.866 (t, terminal –*CH_3*, 6H), 1.264 (m, –CH_3*$(CH_2)_5$*–, 20H), 1.566 (m, –$CH_3(CH_2)_5$*CH_2*–, 4H), 3.227 (m, –$CH_3(CH_2)_5CH_2$*CH_2*–, 4H), 3.459, (m, –NH*CH_2CH_2*NH–, 4H), 3.605 (s, –*CH_3*N^+–, 12H), 4.634 (m, –$(Me)_2^+N$*CH_2*CO–, 8H), 8.234 (br m, amide –*NH*C_8H_{17}, 2H), 8.734 (br m, amide –*NH*CH_2CH_2*NH*–, 2H); HRMS: m/z 285.4176 (calculated), 285.2479 (found), $[M–2Br+H]^{2+}$.

4b: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.859 (t, terminal –*CH_3*, 6H), 1.277 (m, –CH_3*$(CH_2)_5$*– 20H), 1.538 (m, –$CH_3(CH_2)_5$*CH_2*–, 4H), 1.848 (m, –$NHCH_2$*CH_2*CH_2NH–, 2H) 3.241 (m, – $CH_3(CH_2)_5CH_2$*CH_2*–, 4H), 3.377, (m, –NH*CH_2CH_2*CH_2*NH–, 4H), 3.582 (s, –*CH_3*N^+–, 12H), 4.666 (m, –$(Me)_2^+N$*CH_2*CO–, 8H), 8.178 (br m, amide –*NH*C_8H_{17}, 2H), 8.601 (br m, amide –*NH*$CH_2CH_2CH_2$*NH*–, 2H); HRMS: m/z 292.4039 (calculated), 292.2497 (found), $[M–2Br+H]^{2+}$.

4c: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.864 (t, terminal –*CH_3*, 6H), 1.282 (m, –CH_3*$(CH_2)_5$*–, 20H), 1.548 (m, –$CH_3(CH_2)_5$*CH_2*–, 4H), 1.664 (m, –$NHCH_2$*$(CH_2)_2$*CH_2NH–, 4H) 3.232 (m,

–$CH_3(CH_2)_5CH_2CH_2$–, 4H), 3.320, (m, –NH$CH_2(CH_2)_2CH_2$NH–, 4H), 3.582 (s, –CH_3N^+–, 12H), 4.655 (m, –$(Me)_2{}^+NCH_2CO$–, 8H), 8.210 (br m, amide –*NH*C_8H_{17}, 2H), 8.467 (br m, amide –*NH*$CH_2(CH_2)_2CH_2$*NH*–, 2H); HRMS: m/z 299.4442 (calculated), 299.2620 (found), $[M–2Br+H]^{2+}$.

4d: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.871 (t, terminal –CH_3, 6H), 1.290 (m, –$CH_3(CH_2)_5$–, 20H), 1.444 (m, –$CH_3(CH_2)_5CH_2$–, 4H), 1.603 (m, –NH$CH_2(CH_2)_4CH_2$NH–, 8H) 3.249 (m, –$CH_3(CH_2)_5CH_2CH_2$–, 4H), 3.317, (m, –NH$CH_2(CH_2)_4CH_2$NH–, 4H), 3.580 (s, –CH_3N^+–, 12H), 4.637 (m, –$(Me)_2{}^+NCH_2CO$–, 8H), 8.205 (br m, amide –*NH*C_8H_{17}, 2H), 8.489 (br m, amide –*NH*$CH_2(CH_2)_4CH_2$*NH*–, 2H); HRMS: m/z 313.4707 (calculated), 313.2765 (found), $[M–2Br+H]^{2+}$.

5a: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.873 (t, terminal –CH_3, 6H), 1.275 (m, –$CH_3(CH_2)_9$–, 36H), 1.547 (m, –$CH_3(CH_2)_9CH_2$–, 4H), 3.228 (m, –$CH_3(CH_2)_9CH_2CH_2$–, 4H), 3.464, (m, –NHCH_2CH_2NH–, 4H), 3.604 (s, –CH_3N^+–, 12H), 4.617 (m, –$(Me)_2{}^+NCH_2CO$–, 8H), 8.209 (br m, amide –*NH*$C_{12}H_{25}$, 2H), 8.703 (br m, amide –*NH*CH_2CH_2*NH*–, 2H); HRMS: m/z 341.5318 (calculated), 341.3035 (found), $[M–2Br]^{2+}$.

5b: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.863 (t, terminal –CH_3, 6H), 1.265 (m, –$CH_3(CH_2)_9$–36H), 1.520 (m, –$CH_3(CH_2)_9CH_2$–, 4H), 1.820 (m, –NH$CH_2CH_2CH_2$NH–, 2H) 3.203 (m, –$CH_3(CH_2)_9CH_2CH_2$–, 4H), 3.333, (m, –NH$CH_2CH_2CH_2$NH–, 4H), 3.934 (s, –CH_3N^+–, 12H), 4.577 (m, –$(Me)_2{}^+NCH_2CO$–, 8H), 8.190 (br m, amide –*NH*$C_{12}H_{25}$, 2H), 8.470 (br m, amide –*NH*$CH_2CH_2CH_2$*NH*–, 2H); HRMS: m/z 348.5415 (calculated), 348.3115 (found), $[M–2Br]^{2+}$.

5c: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.876 (t, terminal –CH_3, 6H), 1.278 (m, –$CH_3(CH_2)_9$–, 36H), 1.557 (m, –$CH_3(CH_2)_9CH_2$–, 4H), 1.676 (m, –NH$CH_2(CH_2)_2CH_2$NH–, 4H) 3.243 (m, –$CH_3(CH_2)_9CH_2CH_2$–, 4H), 3.325, (m, –NH$CH_2(CH_2)_2CH_2$NH–, 4H), 3.589 (s, –CH_3N^+–, 12H), 4.629 (m, –$(Me)_2{}^+NCH_2CO$–, 8H), 8.197 (br m, amide –*NH*$C_{12}H_{25}$, 2H), 8.488 (br m, amide –*NH*$CH_2(CH_2)_2CH_2$*NH*–, 2H); HRMS: m/z 355.5584 (calculated), 355.3191 (found), $[M–2Br]^{2+}$.

5d: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.873 (t, terminal –CH_3, 6H), 1.298 (m, –$CH_3(CH_2)_9$–, 36H), 1.438 (m, –$CH_3(CH_2)_9CH_2$–, 4H), 1.613 (m, –NH$CH_2(CH_2)_4CH_2$NH–, 8H) 3.219 (m, –$CH_3(CH_2)_9CH_2CH_2$–, 4H), 3.312, (m, –NH$CH_2(CH_2)_4CH_2$NH–, 4H), 3.591 (s, –CH_3N^+–, 12H), 4.639 (m, –$(Me)_2{}^+NCH_2CO$–, 8H), 8.210 (br m, amide –*NH*$C_{12}H_{25}$, 2H), 8.510 (br m,

amide –*NH*$CH_2(CH_2)_4CH_2$*NH*–, 2H); HRMS: m/z 369.5850 (calculated), 369.3349 (found), $[M–2Br]^{2+}$.

6a: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.879 (t, terminal –*CH*$_3$, 6H), 1.295 (m, –CH_3*(CH$_2$)$_{13}$*–, 52H), 1.564 (m, –$CH_3(CH_2)_{13}$*CH*$_2$–, 4H), 3.256 (m, –$CH_3(CH_2)_{13}CH_2$*CH*$_2$–, 4H), 3.482, (m, –NH*CH*$_2$*CH*$_2$NH–, 4H), 3.608 (s, –*CH*$_3$$N^+$–, 12H), 4.596 (m, –$(Me)_2^+N$*CH*$_2$CO–, 8H), 8.268 (br m, amide –*NH*$C_{16}H_{33}$, 2H), 8.858 (br m, amide –*NH*CH_2CH_2*NH*–, 2H); HRMS: m/z 397.6382 (calculated), 397.3664 (found), $[M–2Br]^{2+}$.

6b: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.875 (t, terminal –*CH*$_3$, 6H), 1.277 (m, –CH_3*(CH$_2$)$_{13}$*–52H), 1.550 (m, –$CH_3(CH_2)_{13}$*CH*$_2$–, 4H), 1.883 (m, –$NHCH_2$*CH*$_2$$CH_2NH$–, 2H) 3.241 (m, –$CH_3(CH_2)_{13}CH_2$*CH*$_2$–, 4H), 3.392, (m, –NH*CH*$_2$$CH_2$*CH*$_2$NH–, 4H), 3.588 (s, –*CH*$_3$$N^+$–, 12H), 4.645 (m, –$(Me)_2^+N$*CH*$_2$CO–, 8H), 8.119 (br m, amide –*NH*$C_{16}H_{33}$, 2H), 8.636 (br m, amide –*NH*$CH_2CH_2CH_2$*NH*–, 2H); HRMS: m/z 404.6514 (calculated), 404.3876 (found), $[M–2Br]^{2+}$.

6c: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.879 (t, terminal –*CH*$_3$, 6H), 1.278 (m, –CH_3*(CH$_2$)$_{13}$*–, 52H), 1.563 (m, –$CH_3(CH_2)_{13}$*CH*$_2$–, 4H), 1.645 (m, –$NHCH_2$*(CH$_2$)$_2$*CH_2NH–, 4H) 3.252 (m, –$CH_3(CH_2)_{13}CH_2$*CH*$_2$–, 4H), 3.345, (m, –NH*CH*$_2$$(CH_2)_2$*CH*$_2$NH–, 4H), 3.589 (s, –*CH*$_3$$N^+$–, 12H), 4.606 (m, –$(Me)_2^+N$*CH*$_2$CO–, 8H), 8.208 (br m, amide –*NH*$C_{16}H_{33}$, 2H), 8.510 (br m, amide –*NH*$CH_2(CH_2)_2CH_2$*NH*–, 2H); HRMS: m/z 411.6647 (calculated), 411.3818 (found), $[M–2Br]^{2+}$.

6d: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.878 (t, terminal –*CH*$_3$, 6H), 1.249 (m, –CH_3*(CH$_2$)$_{13}$*–, 52H), 1.454 (m, –$CH_3(CH_2)_{13}$*CH*$_2$–, 4H), 1.614 (m, –$NHCH_2$*(CH$_2$)$_4$*CH_2NH–, 8H) 3.252 (m, –$CH_3(CH_2)_{13}CH_2$*CH*$_2$–, 4H), 3.340, (m, –NH*CH*$_2$$(CH_2)_4$*CH*$_2$NH–, 4H), 3.585 (s, –*CH*$_3$$N^+$–, 12H), 4.607 (m, –$(Me)_2^+N$*CH*$_2$CO–, 8H), 8.202 (br m, amide –*NH*$C_{16}H_{33}$, 2H), 8.492 (br m, amide –*NH*$CH_2(CH_2)_4CH_2$*NH*–, 2H); HRMS: m/z 425.6913 (calculated), 425.4066 (found), $[M–2Br]^{2+}$.

7: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.850 (t, terminal –*CH*$_3$, 3H), 1.259 (m, –CH_3*(CH$_2$)$_5$*–, 10H), 1.603 (m, –$CH_3(CH_2)_5$*CH*$_2$–, 2H), 3.312 (m, –CONH*CH*$_2$–, 2H), 3.488 (s, –(*CH*$_3$)$_3$$N^+$–, 9H), 4.681 (s, –$(CH_3)_3^+N$*CH*$_2$CO–, 2H), 8.652 (br s, amide –*NH*, 1H); HRMS: m/z 229.3822 (calculated), 229.2018 (found), $[M–Br]^+$.

8: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.859 (t, terminal –*CH*$_3$, 3H), 1.251 (m, –CH_3*(CH$_2$)$_9$*–, 18H), 1.556 (m, –$CH_3(CH_2)_9$*CH*$_2$–, 2H), 3.229 (m, –CONH*CH*$_2$–, 2H), 3.481 (s,

–(CH_3)$_3$N$^+$–, 9H), 4.672 (s, –(CH$_3$)$_3^+$NCH_2CO–, 2H), 8.601 (br s, amide –*NH*, 1H); HRMS: m/z 285.4885 (calculated), 285.3010 (found), [M–Br]$^+$.

9: ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.871 (t, terminal –CH_3, 3H), 1.249 (m, –CH$_3$$(CH_2)_{13}$–, 26H), 1.549 (m, –CH$_3$(CH$_2$)$_{13}$$CH_2$–, 2H), 3.220 (m, –CONH$CH_2$–, 2H), 3.459 (s, –($CH_3$)$_3N^+$–, 9H), 4.663 (s, –(CH$_3$)$_3^+NCH_2$CO–, 2H), 8.599 (br s, amide –*NH*, 1H); HRMS: m/z 341.5948 (calculated), 341.3529 (found), [M–Br]$^+$.

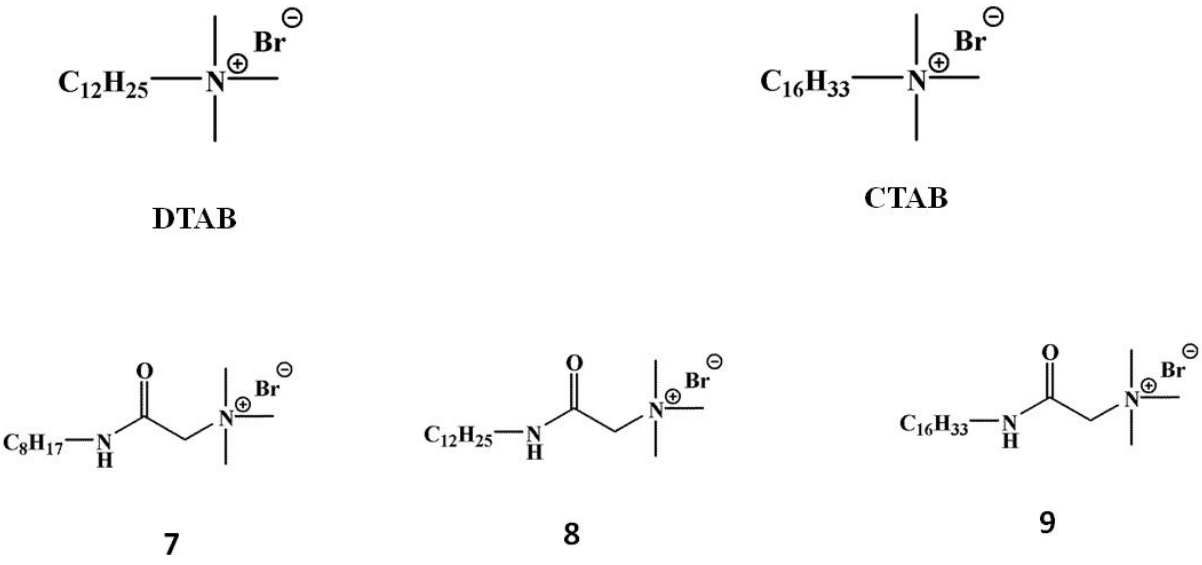

Figure S1. Structures of various monomeric surfactants without or with the amide functionality used in this study.

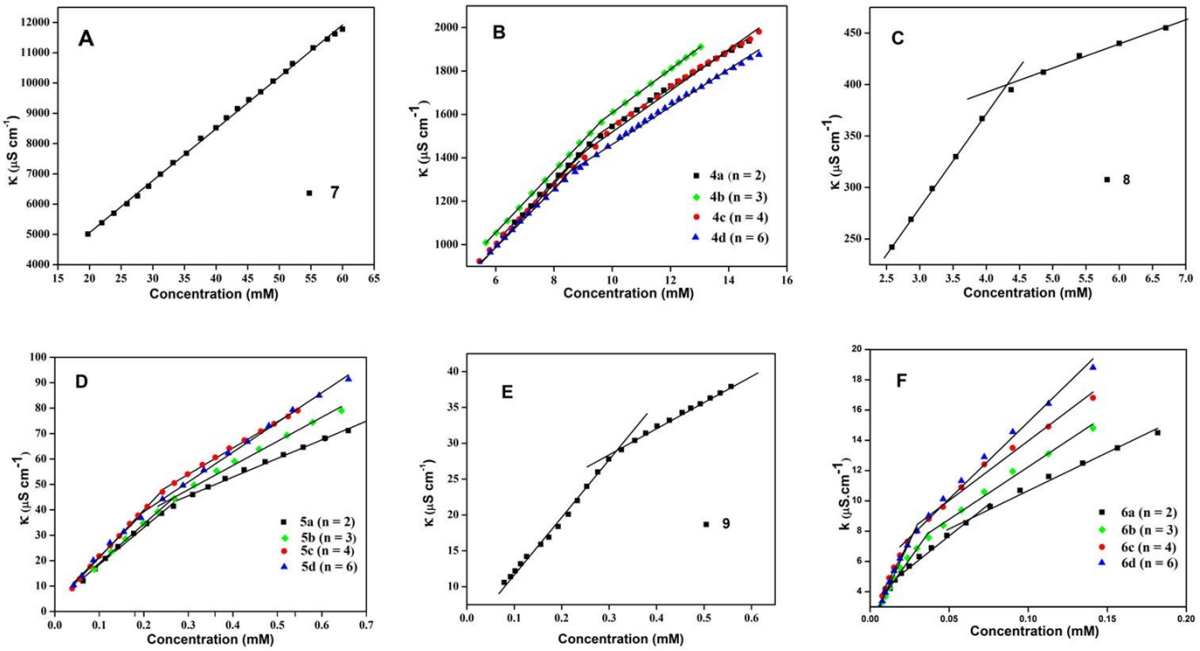

Figure S2. Plot of electrical conductivity (κ) *vs.* surfactant concentrations in H_2O: (A, C, E) for monomeric surfactants (**7**, **8**, and **9**) and (B, D, and F) for gemini surfactants (**4a−4d**, **5a-5d**, and **6a-6d**).

Table S1. Degree of ionization (α), scattering length density and volume of surfactant monomer for cationic amide bearing surfactants

Surfactant	Degree of ionization[a] (α)	Scattering length density[b] ($\times 10^{10}$ cm^{-2})	Volume of surfactant[c] (Å^3)
4a (n = 2)	0.61	0.480	1134.8
4b (n = 3)	0.70	0.460	1163.0
4c (n = 4)	0.65	0.440	1191.2
4d (n = 6)	0.64	0.410	1247.6
5a (n = 2)	0.50	0.300	1350.0
5b (n = 3)	0.60	0.290	1378.2
5c (n = 4)	0.55	0.270	1406.4
5d (n = 6)	0.66	0.250	1462.8
6a (n = 2)	0.60	0.210	1565.2
6b (n = 3)	0.47	0.210	1593.4
6c (n = 4)	0.40	0.200	1621.6
6d (n = 6)	0.45	0.180	1678.0
7	ND	0.056	435.7
8	0.27	-0.016	543.3
9	0.40	-0.065	650.9

[a]Degree of ionization was determined by electrical conductivity method. [b]Scattering length density for all the surfactants was calculated from SANS study. [c]Volume of the surfactants was calculated by using Tanford's formula and others.[1-3] ND = Not determined.

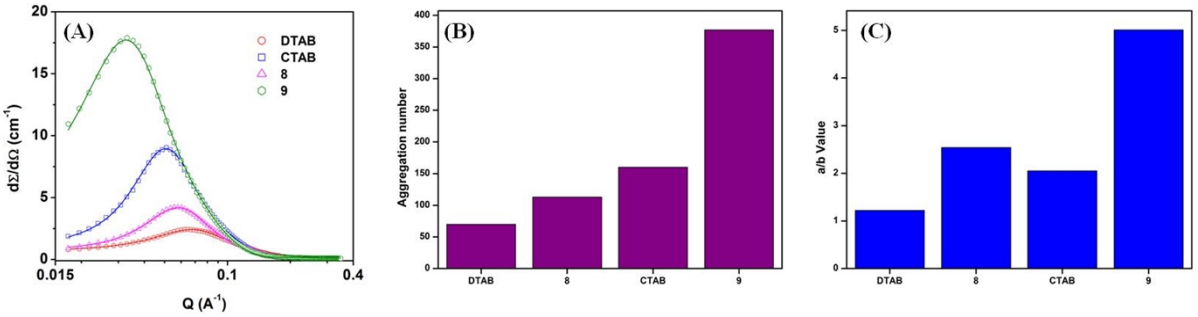

Figure S3. SANS distributions of aqueous solution of the monomeric surfactants (**DTAB, CTAB, 8,** and **9**) at 100 mM concentration at 30 °C. The lines shown are theoretical fits and the solid marks are experimentally determined data points (A). Effect of the amide bonds on the aggregation properties of the monomeric surfactants: (B) effect on the aggregation number; (C) effect on the ratio of semimajor axis (a) to semiminor axis (b).

2. Analysis of SANS Data. The aggregation number N for the micelle is related to the micellar volume V_m by the relation $N = V_m/v$, where v is the volume of the individual surfactant molecule. The ranges molecular volumes of the surfactants **4a-4d, 5a-5d,** and **6a-6d** (n = 2, 3, 4, and 6) were 1134.8-1247.6, 1350.0-1462.8, and 1565.2-1678.0 Å^3 respectively (Table S1). The molecular volumes of the monomeric surfactants **7**, **8**, and **9** were found to be 435.7, 543.3, and 650.9 Å^3 respectively. Volume of all the monomeric surfactants bearing amide group (**7**, **8**, and **9**) was calculated as follows:

$$V_{total} = (V_{hc} + V_{hg} + V_{linker})$$

where V_{hc} is the volume of the $-C_7H_{14}$,$-C_{11}H_{23}$, or $-C_{15}H_{31}$ hydrocarbon tail (calculated by Tanford's formula[34] and found to be 215.7, 323, 430.9 Å^3), V_{hg}, volume of the head group is 102 Å^3 (as taken from the literature[28-30]) and V_{linker}, volume of linker ($-CH_2NHCOCH_2-$) part is 118 Å^3 ($V_{linker} = M/dN_A$, where M = 71 is the molecular weight of the linker, d = 1 g.cm^{-3} is the density , and N_A is the Avogadro's Number).[35] The volume of the gemini surfactants **4a-4d, 5a-5d,** and **6a-6d** were calculated as follows:

$$V_{total} = [2\ \{V_{hc} + (2\times V_{CH3}) + V_N + (2\times V_{linker})\} + \{(n-2) \times V_{CH2})\}]$$

where V_{hc}, volume of the $-C_7H_{14}$,$-C_{11}H_{23}$, or $-C_{15}H_{31}$ hydrocarbon chains as calculated before; V_{linker}, volume of linker ($-CH_2NHCOCH_2-$) part is 118 Å^3; V_{CH3} = 42.6 Å^3 is the volume of the methyl groups attached to quaternized nitrogen atom has been taken from the literature;[36] V_N = 30.5 Å^3 is the volume of quaternized nitrogen atom; V_{CH2} = 28.2 Å^3 is the volume of the methylene groups (spacer, n).

The coherent differential scattering cross section, $d\Sigma/d\Omega$, can be reduced for an assembly of monodispersed micelles as given by

$$d\Sigma/d\Omega = nV_m^2(\rho_m-\rho_s)^2P(Q)S(Q) \qquad (1)$$

The equation 1 can also be rewritten as follows.

$$d\Sigma/d\Omega = cN(b_m-v\rho_s)^2P(Q)S(Q) \qquad (2)$$

where c $(= nN)$ is the surfactant concentration and b_m $(= \rho_m v)$ is the total coherent scattering amplitude of the surfactant molecule.

The form factor $P(Q)$ for an ellipsoidal particle is given by

$$P(Q) = \int [F(Q,\mu)]^2\, d\mu \qquad (3)$$

where $F(Q)$ is calculated as

$$F(Q,\mu) = 3(\sin w - w\cos w)/w^3 \qquad (4)$$

$$w = Q[a^2\mu^2 + b^2(1 - \mu^2)]^{1/2} \qquad (5)$$

where *a* and *b* are respectively the semimajor and semiminor axes of the ellipsoid of revolution. μ is the cosine of the angle between *a* and *Q*.

3. Calculations of molecular volumes of the monomeric surfactants:

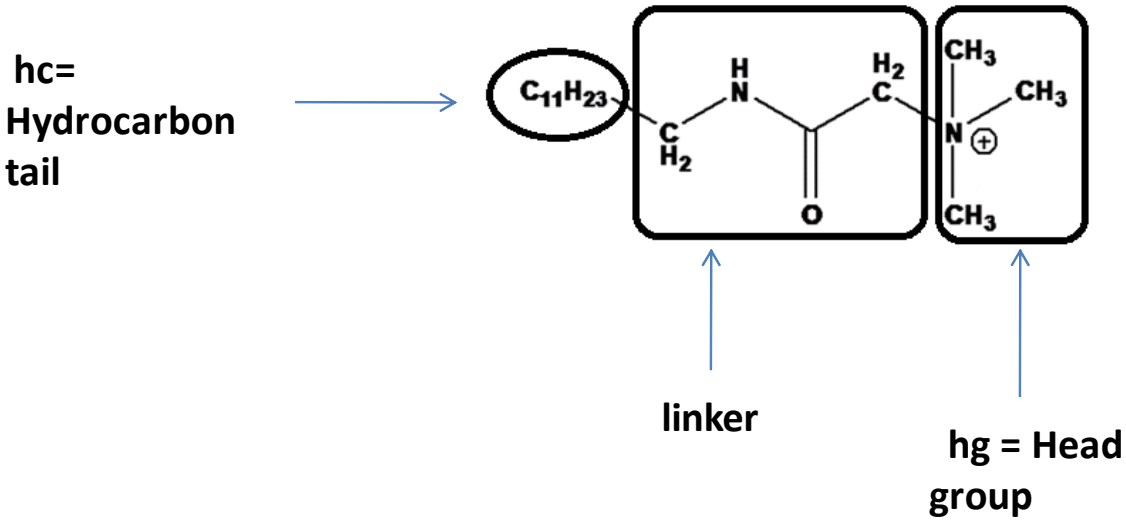

Figure S5. A schematic representation of the various parts of a monomeric surfactant for the determination of molecular volumes.

Molecular Volume of Monomeric Surfactants:

$$V_{total} = (V_{hc} + V_{hg} + V_{linker})$$

V_{hc}, volume of the hydrocarbon chain is calculated based on Tanford's formula.[1] V_{hg}, volume of the head group is 102 Å^3, as taken from the literature and the volume of linker (–$CH_2NHCOCH_2$–) part is 118 Å^3 (volume of the linker, $V_{linker} = M/d.\ N_A$, where M = 71 is the molecular weight of the linker , d = 1 g cm^{-3} is the density , and N_A is the Avogadro's Number).[2,3]

4. Calculations of molecular volumes of the gemini surfactants:

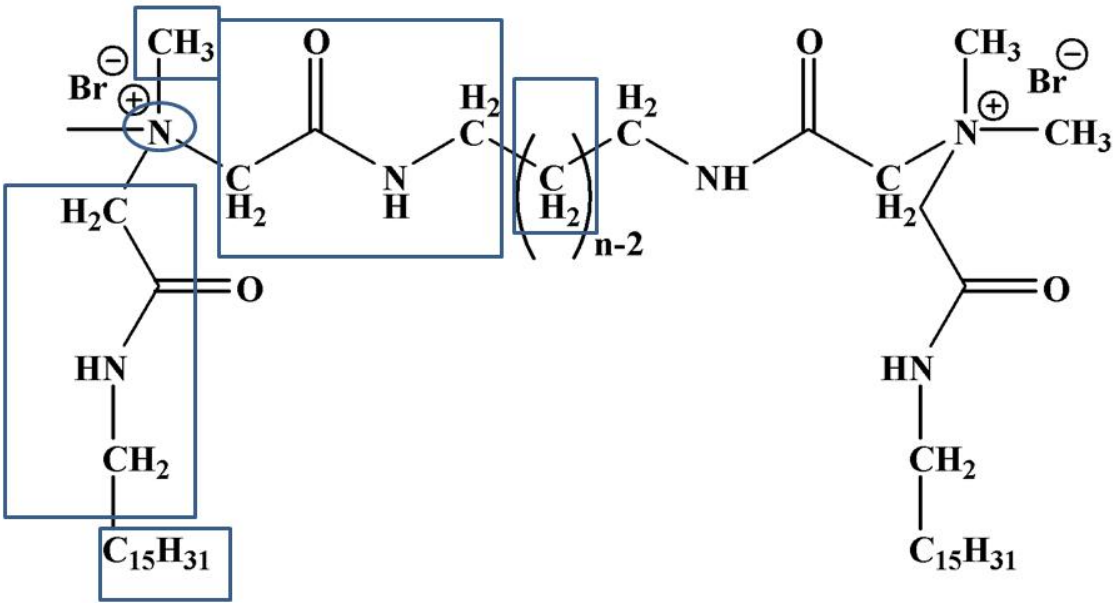

Figure S6. A schematic representation showing different parts of a gemini surfactant for the determination of molecular volumes.

Molecular Volume of Gemini Surfactants:

$$\mathbf{V_{total} = [2\ \{V_{hc} + (2\times V_{CH3}) + V_N + (2\times V_{linker})\} + \{(n-2) \times V_{CH2})\}]}$$

V_{hc}, volume of the hydrocarbon chain is calculated based on Tanford's formula. The volume of linker (– $CH_2NHCOCH_2$–) part is 118 Å^3 (volume of the linker, $V_{linker} = M/d.\ N_A$, where M = 71 is the molecular weight of the linker , d = 1 g cm^{-3} is the density , and N_A is the Avogadro's Number). V_{CH3} = 42.6 Å^3 is the volume of the methyl groups attached to quaternized nitrogen atom and has been taken from the literature. V_N = 30.5 Å^{3}is the volume of quaternized nitrogen atom. V_{CH2} = 28.2 Å^{3}is the volume of the mehtylene groups (spacer).[2,3]

5. Structure factor for interacting micelles. The interparticle structure factor $S(Q)$ has been found to depend on the spatial distribution of the micelles. Unlike the calculation of P(Q), it is quite complicated to calculate S(Q) for any other shape than spherical. This is because of S(Q) depends on the shape as well as on the orientation of the particles and there are no analytical expressions available to calculate it for asymmetric particles. To simplify this, prolate ellipsoidal micelles are usually assumed to be equivalent as spherical. In the following analysis, we have calculated $S(Q)$ using rescaled mean spherical approximation as developed by Hansen and Hayter.[30] The ellipsoidal micelle is approximated by an equivalent sphere of radius $R = (ab^2)^{1/3}$, the intermicellar interaction is modelled via a screened Coulomb potential and $S(Q)$ under mean spherical approximation. In this analysis, the only unknown parameter in $S(Q)$ is the effective monomer charge, α.

6. CMC of gemini surfactant in D_2O by Conductivity Method: The CMC of the surfactant 5c in D_2O as a solvent was determined similarly as it is for H_2O (described in the main article).

7. CMC of gemini surfactant by Steady State Fluorescence Method: Pyrene, a micelle-soluble hydrophobic fluorescence probe, exhibits fine structure in its steady-state fluorescence emission spectra having five vibronic peaks. The nature and the intensity of such fine-structured bands are quite dependent on the polarity of the environment. The first (I_1) and third vibronic peaks (I_3) show the greatest solvent dependency.[5,6] Pyrene solution was made by dissolving pyrene (5 mg) in 10 mL of methanol followed by dilution with deionized water to obtain a 2 mM stock solution. This solution (2 μL, 2 mM) was added to 2 mL of surfactant solution at various concentrations each time. Excitation wavelength was fixed at 334 nm and emission spectra of the region 350-460 nm were recorded keeping the bandwidths fixed at 2.5 nm and 8 nm respectively for the emission and the excitation. The ratio (I_1/I_3) was plotted against concentration (Figure S7C and S7D) followed by a sigmoidal fitting. The curves show a decrease in the quotient intensities of both vibrational peaks when micelles are formed and the centre of the sigmoid was considered as the CMC.[6]

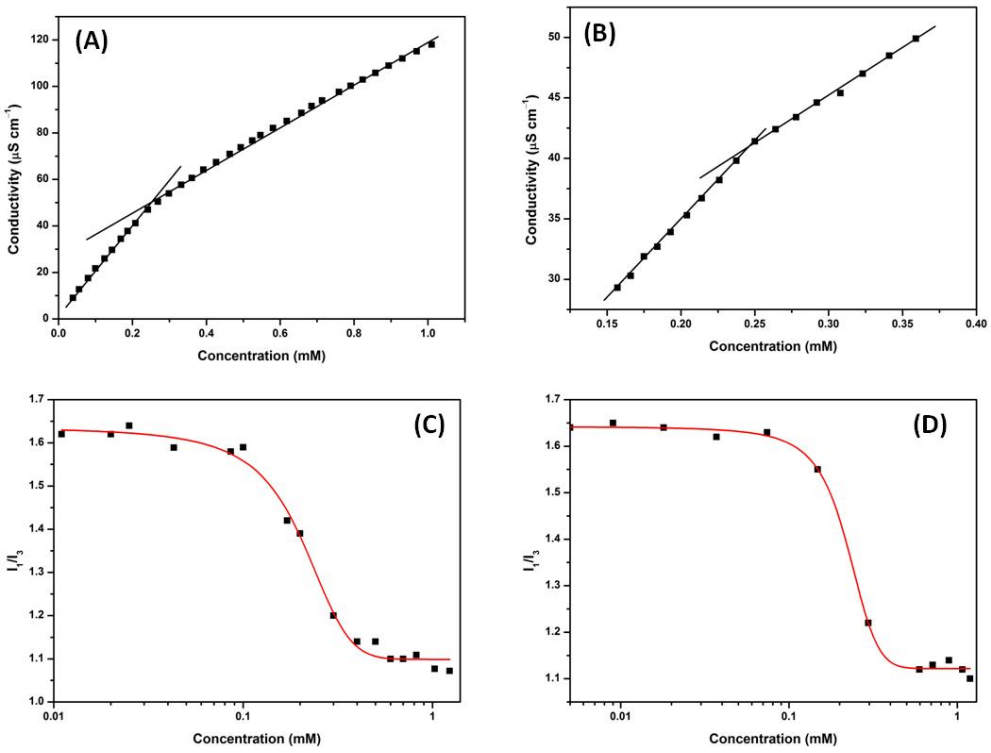

Figure S7. Plot of electrical conductivity *vs.* surfactant concentrations both in H_2O and D_2O for gemini surfactant **5c** (n = 4) (A and B); plot of I_1/I_3 *vs.* surfactant concentrations both in H_2O and D_2O for gemini surfactant **5c** (n = 4) (C and D).

7. Enzymatic Hydrolysis. 20 μL of a 125 mM solution of the surfactant (**4c**, n = 8) in D_2O was added to 480 μL of enzyme trypsin/PBS buffer solution (pH 7.2) in a 5-mm NMR tube. The enzyme content was 1300 units for trypsin. The buffer solution was prepared from D_2O and non-deuterated phosphate salts. The tubes were held in a water bath at 37 °C, where proton NMR spectra were recorded at day 1, 5 and 10 on Bruker AMX 400 MHz spectrometer (Figure S8). The extent of hydrolysis, during 16 days at 37°C, was determined by ^{1}HNMR analysis of the enzyme-containing solution of the surfactant. It was found that the amide containing surfactant hydrolysed at day 1 and the extent of hydrolysis was found to be 25-35% at day 16.

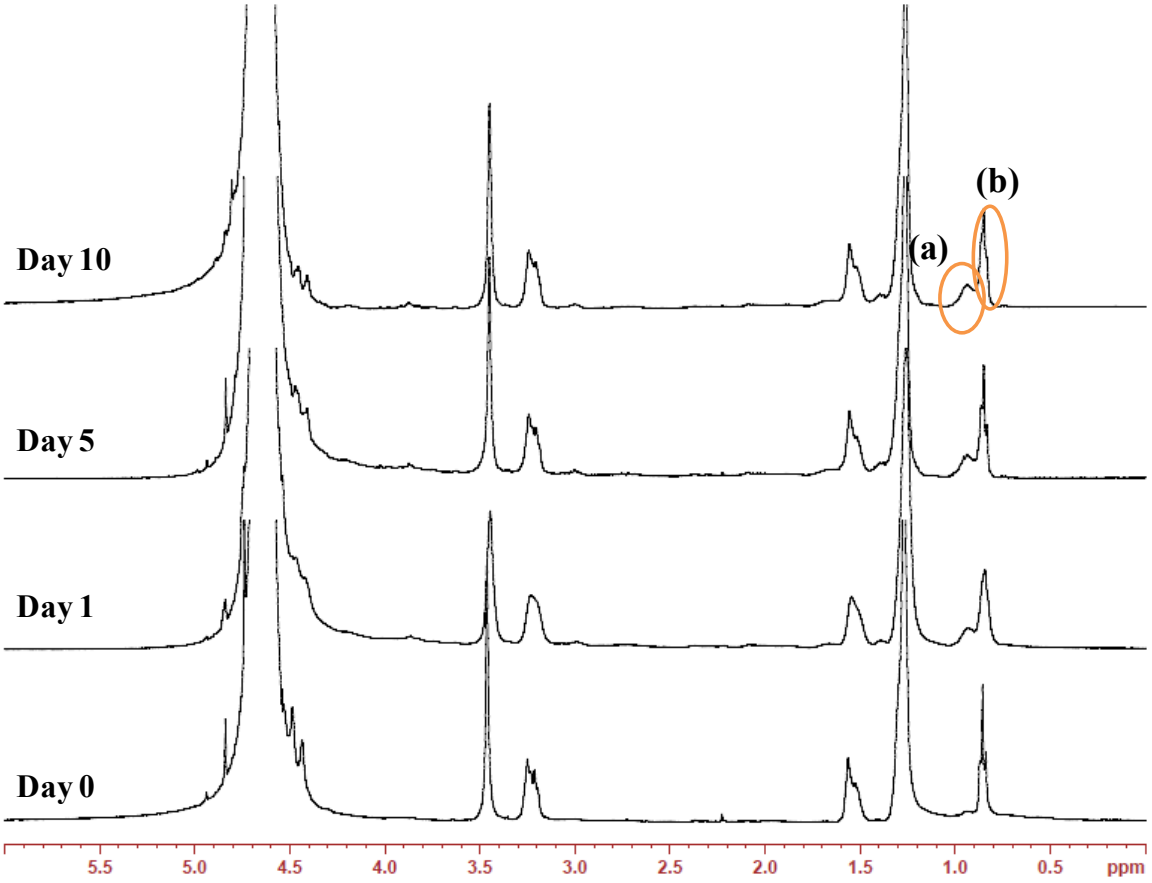

Figure S8. ^{1}HNMR Spectra of enzymatic degradation of the amide-containing cationic dimeric amphiphile (**4c**) under enzyme trypsin. (a) Corresponds to the peak of –C*H*$_3$ protons of the hydrolysed octyl amine, one of the hydrolysed products of **4c**; (b) Corresponds to the peak of the –*CH*$_3$ protons of the octyl long chain of the surfactants.

8. Alkaline Hydrolysis (Chemical Hydrolysis). 50 µL of a 100 mM solution of the surfactant **4d** in D_2O was added to 450 µL of 1.2 M NaOD/D_2O solution in a NMR tube. The tubes were held in a water bath at 37 °C, where proton NMR spectra were recorded at day 1, 5 and 10 on a Bruker AMX 400 MHz spectrometer (Figure S9).The extent of hydrolysis was determined by ^{1}HNMR analysis of the surfactant solution. It was found that the amide containing surfactant hydrolysed even at day 1 under alkaline condition and the extent of hydrolysis was found to be 45-55% at day 10. The alkaline hydrolysis of the amide containing surfactant was confirmed by the appearance of α–C*H*$_2$ protons of the hydrolysed amines at ~2.55 ppm in the ^{1}HNMR spectrum. Also it was observerd that intensity of the peak corresponds to α–*CH*$_2$ protons of amide groups in unreacted surfactant decreases with time which further indicated that the amide containing surfactant degraded in the presence of

base. These results thus indicated that the presence of the ammonium group in alpha to the C=O gave degradation under basic conditions (Figure S10).

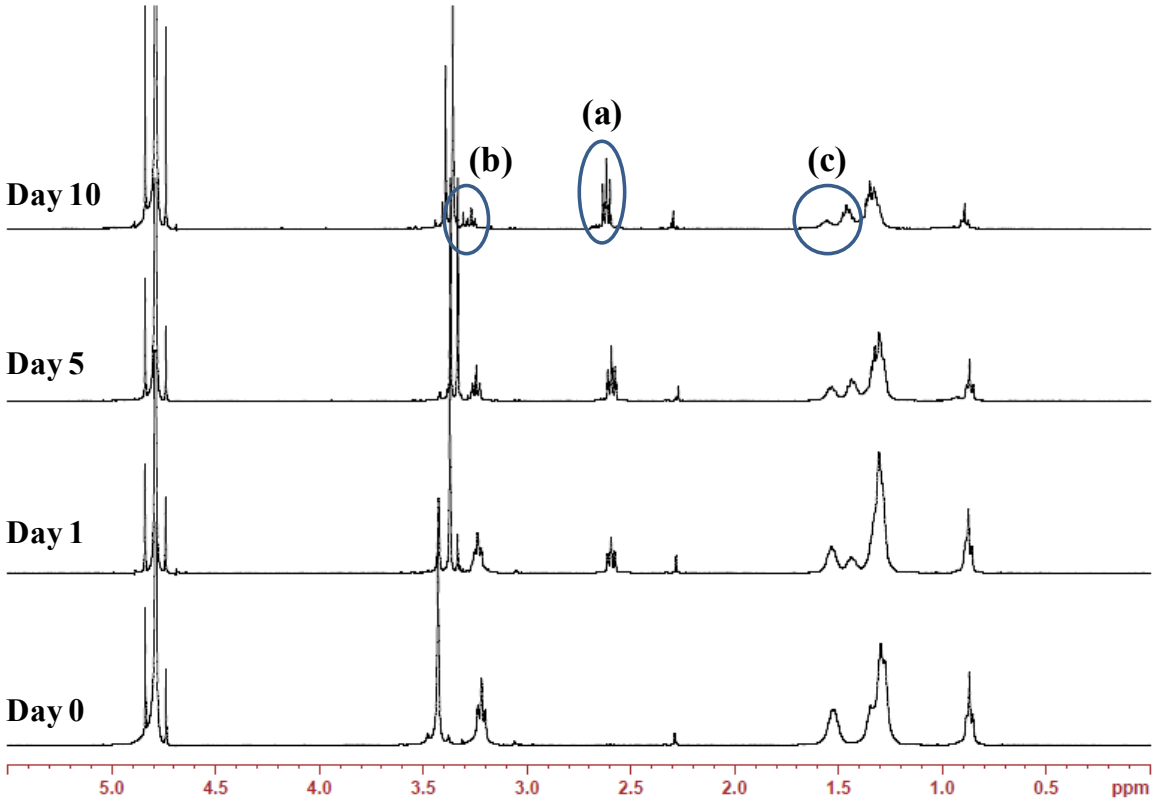

Figure S9. ^{1}HNMR Spectra of alkaline hydrolysis of the amide-containing cationic gemini surfactant (**4d**) in the presence of NaOD. (a) Corresponds to the peak of α–CH_2 protons of the hydrolysed amines, one of the hydrolysed products of **4d**; (b) Corresponds to the peak of the α–CH_2 protons of amide groups in unreacted surfactant; (c) Corresponds to the peak of the β–CH_2 protons of amide groups in unreacted surfactant and hydrolysed amine.

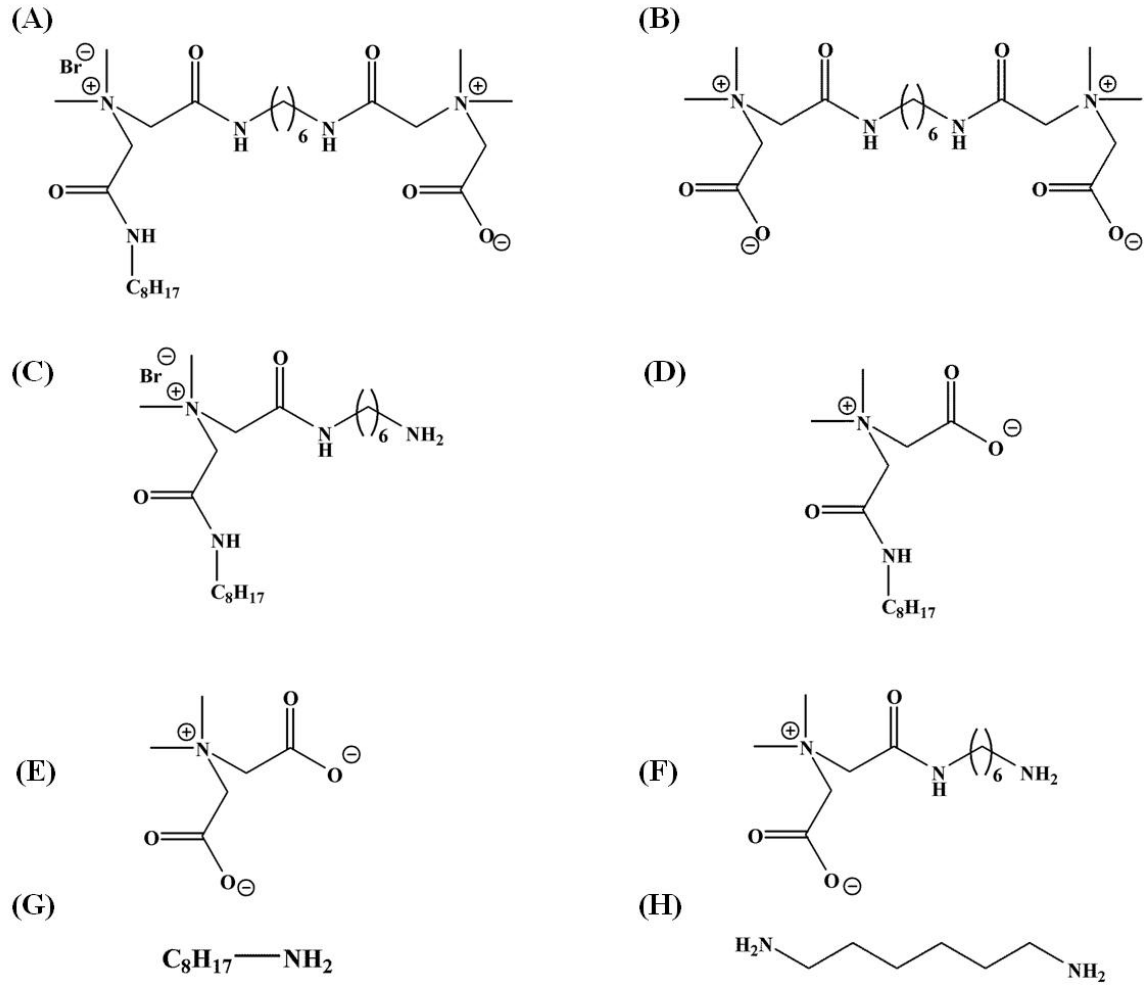

Figure S10: Possible hydrolysed products of the surfactant **4d** (n = 6): (A, B and G) possible hydrolysed products after degradation of the side chain amide bonds; (C, D and H) possible hydrolysed products after degradation of the amide bonds present in the spacer; (E, F, G and H) possible hydrolysed products after degradation of the amide bonds both in the spacer and long chain.

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