Section-5.2: Synthesis, Characterization and Surface properties of Cationic Piperidinium and Morpholinium based Surfactants.

Section-5.2.1: Synthesis and Characterization of Cationic Piperidinium and Morpholinium based Surfactants.

Section-5.2.2: Evaluation of Surface properties of Piperidinium and Morpholinium based Surfactants.

Section-5.2.3: Evaluation of Thermal stability of Piperidinium and Morpholinium based Surfactants by thermogravimetry analysis.
Section 5.2.1: Synthesis and characterization of Cationic Piperidinium and Morpholinium based Surfactants.

Result and discussion:

Cationic surfactants bearing piperidine and morpholine headgroups have been synthesized via regioselective nucleophilic substitution reaction using zinc perchlorate as catalyst (Scheme 5.2). 1,2-Epoxydodecane (1), 1,2-Epoxytetradecane (2) and 1,2-Epoxyhexadecane (3) on reaction with piperidine (4) and morpholine (5) gave the corresponding β-amino alcohols (6-11) which were then quaternized with 2-bromo ethanol (12) to get respective cationic surfactants (13-18).

The structure of piperidinium and morpholinium based cationic surfactants have been established by $^1$H, $^{13}$C, DEPT (Distortionless enhanced polarization transfer), 2D HETCOR (Heteronuclear chemical shift correlation) and 2D COSY (Correlation Spectroscopy) experiments. In $^1$H spectra (Figure 5.2.1 and Figure 5.2.2) terminal protons of the cationic piperidinium (13-15) and morpholinium surfactants (16-18) were observed as triplet between δ 0.84-0.90 ppm. The ring protons of piperidine were observed at δ 1.76-1.96 and 3.41-3.87 ppm. In case of morpholinium surfactants (Figure 5.2.2) the ring protons have been observed...
Figure 5.2.1: $^1$H spectra of 1-(2-Hydroxyethyl)-1-(2-hydroxytetradecyl)piperidin-1-ium bromide (14).

Figure 5.2.2: $^1$H spectra of 4-(2-Hydroxyethyl)-4-(2-hydroxyhexadecyl)morpholin-4-ium bromide (18).

between $\delta$ 3.47-3.87 and 3.89-4.15 ppm. The methylene protons (i.e. $^+\text{NCH}_2\text{CH(OH)}$), attached directly to positively charged heteroatom (nitrogen) are non-equivalent in nature, they were observed as a pair of multiplets at $\delta$ 3.12-3.53 ($H_a$) and 3.47-3.87 ($H_b$) ppm in all
cationic surfactants (13-18). However, the methylene protons (i.e., $^+\text{NCH}_2\text{CH}_2\text{OH}$), directly attached to positively charged nitrogen atom were observed as a multiplets between $\delta$ 3.52-3.77 ppm for piperidinium surfactants at $\delta$ 3.89-4.15 ppm for morpholinium surfactants. The methine proton, which attached directly to hydroxyl group (i.e., $\text{-CH-OH}$) has been observed in the range of $\delta$ 4.12-4.33 ppm for all cationic surfactants. The signal for methylene protons, directly attached to hydroxyl group (i.e., $^+\text{NCH}_2\text{CH}_2\text{OH}$) appeared as multiplet between $\delta$ 3.86-4.06 ppm for piperidinium cationics and $\delta$ 3.89-4.15 ppm in case of morpholinium cationics.

**Figure 5.2.3:** $^{13}$C spectra of 4-(2-Hydroxyethyl)-4-(2-hydroxyhexadecyl)morpholino-4-ium bromide (18).

In the $^{13}$C NMR (Figure 5.2.3) spectra the $sp^3$ terminal methyl carbon were observed at $\delta$ 14.00-14.16 ppm. The $sp^3$ carbon of $\text{-CH}_2$ chain were observed in the range of $\delta$ 20.07-36.75 ppm. The carbon directly attached to the heterocyclic positively charged piperidine and morpholine nitrogen (i.e., $^+\text{NCH}_2\text{CH}_2\text{OH}$) was observed at $\delta$ 60.65-61.56 ppm. The second $sp^2$ hybridised carbon (i.e $^+\text{NCH}_2\text{CH(OH)}$), also attached to heteroatom (nitrogen) was observed at $\delta$ 63.76-64.91 ppm. These carbons were identified on the bases of DEPT-135 (Figure 5.2.4) spectra of the same molecule which appeared as negative signals in the spectra. The signal for carbons bearing hydroxyl group (i.e $\text{HOCH}_2\text{CH}_2\text{N}^+$ and $\text{-CH-OH}$) were observed at $\delta$ 61.78-62.56 ppm and $\delta$ 65.08-65.65 ppm, respectively. The methine
carbon bearing the hydroxyl group (i.e., -CH-OH) was observed as a positive signal in DEPT-135 spectra.

Figure 5.2.4: $^{13}$C/DEPT-135 spectra of 4-(2-Hydroxyethyl)-4-(2-hydroxyhexadecyl)morpholin-4-i um bromide (18).

Figure 5.2.5: 2D HETCOR ($^1$H-$^{13}$C) 4-(2-Hydroxyethyl)-4-(2-hydroxyhexadecyl)morpholin-4-i um bromide (18).
The structure of these cationic surfactants has further been established by ESI-MS (Positive ion) mass spectroscopy. The parent ion peak for piperidinium cationic surfactants (13-15) have been observed at 314.3, 342.3, 370.3 and for morpholinium cationics (16-18) the same has been observed at 316.3, 344.3, 372.3 respectively. These signals account for the loss of bromide ion from the respective cationic surfactants (13-18), leading to the formation of parent ion (M⁺-Br). The (M⁺-Br)+1 and (M⁺-Br)+2 peaks were also observed in each case.

**Experimental:**

**Materials and methods**

1,2-Epoxydodecane, 1,2-Epoxytetradecane, 1,2-Epoxyhexadecane and Zinc perchlorate hexahydrate were purchased from Sigma Aldrich, USA and were used without any purification. Piperidine, Morpholine and 2-Bromo ethanol were purchased from Central Drug House, New Delhi, India. Millipore water was used in all experiments.

Infrared (IR) spectra were recorded as a thin neat film on a Fourier transform infrared (FT-IR) instrument (Model 8400s, Shimadzu, Kyoto, Japan). Mass spectra were recorded on Waters Q-Tof Micromass equipment using ESI as ion source. ¹H and ¹³C NMR spectra were...
recorded on a JEOL AL-300 (JEOL Japan), FT-NMR 300 MHz system and a BRUKER AVANCE II (Switzerland), FT- NMR 400 MHz system as a solution in CDCl₃, using tetramethylsilane (TMS) as an internal standard.

**Synthesis and Characterisation:** Synthesis of pipridinium and morpholinium based cationic surfactants involved two steps. First step involved a regioselective synthesis of β-amino alcohols (6-11) by using the methodology explained in the previous chapters. 1,2-Epoxydodecane (1), 1,2-Epoxytetradecane (2) and 1,2-Epoxyhexadecane (3) were stirred magnetically with piperidine (4) and morpholine (5) in the presence of catalytic amount of zinc perchlorate hexahydrate at 80 °C for 1 hour under solvent free conditions. The progress of reaction was monitored by thin layer chromatography [Silica gel G coated (0.25mm thick) glass plates, using hexane:ethyl acetate (in a ratio of 90:10 or 85:15) as the mobile phase; the spots were visualised by iodine]. The intermediates β-amino alcohols (6-11) were purified by column chromatography using silica gel (60-120 mesh) as stationary phase and eluting with hexane:ethyl acetate (95:5) solvent system. The isolated yield of pure product as a single isomer is 75-80%. The second step involved quaternization of β-amino alcohols (6-11) with 2-bromo ethanol (12) at 100 °C for 10 hour (Scheme – 5.2). The resulting crude mixtures were cooled to 25 °C. The product was washed thrice with 50 ml of diethyl ether and cold precipitated in acetone to get respective pipridinium and morpholinium based cationic surfactants (13-18).

1-(Piperidin-1-yl)dodecan-2-ol (6). Viscous brown; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.83-0.88 (t, 3H, terminal CH₃), 1.24-1.48 (m, 20H, chain CH₂, CH₂ α to CH-OH and 4 CH₂ of ring), 1.70 (m, 4H, 3, 5 CH₂ of ring), 2.38-2.53 (m, 5H, -CH₂H₅-N and 2, 6 CH₂ of ring), 2.75 (br.s, 2H, -CH₂H₅-N and OH), 3.80 (m, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.07 (+ve, terminal CH₃), 22.64-35.00 (-ve, CH₂ chain and C-3, C-4, C-5 of ring), 54.60 (-ve, C-2 and C-6 of ring), 64.89 (-ve, -CH₂-N), 66.04 (+ve, -CH-OH). IR (CHCl₃) cm⁻¹: 3455, 2928, 1459, 1307, 1115, 876, 781, 725. MS m/z (parent ions): 270.29 and 271.29 (M⁺+1 and M⁺+2).

1-(Piperidin-1-yl)tetradecan-2-ol (7). White solid; NMR (CDCl₃): δ (ppm) 0.84-0.89 (t, 3H, terminal CH₃), 1.25 (br.s, 20H, chain CH₂), 1.33-1.46 (m, 4H, CH₂ α to CH-OH and 4 CH₂ of ring), 1.49-1.62 (m, 4H, 3, 5 CH₂ of ring), 2.14-2.20 (t, 1H, -CH₂H₅-N), 2.25-2.99 (m, 3H, -CH₂H₅-N and 2 CH₂ of ring), 2.58 (br.s, 2H, 6 CH₂ of ring), 3.53 (br.s, 1H, OH), 3.60-3.67 (m, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.09 (+ve,
terminal CH$_3$), 22.67-35.04 (-ve, CH$_2$ chain and C-3, C-4, C-5 of ring), 54.64 (-ve, C-2 and C-6 of ring), 64.94 (-ve, -CH$_2$N), 66.08 (+ve, -CH-OH). IR (CHCl$_3$) cm$^{-1}$: 3451, 2926, 1460, 1308, 1044, 878, 781, 725; MS m/z (parent ions): 298.33 and 299.33 (M$^+$+1 and M$^+$+2).

1-(Piperidin-1-yl)hexadecan-2-ol (8). White solid; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.89-0.94 (t, 3H, terminal CH$_3$), 1.29-1.51 (m, 28H, chain CH$_2$, CH$_2$ α to CH-OH and 4 CH$_2$ of ring), 1.75 (m, 4H, 3, 5 CH$_2$ of ring), 2.30-2.44 (m, 4H, -CH$_2$H$_5$N, -CH$_2$H$_8$N and 2 CH$_2$ of ring), 2.73 (br.s, 2H, 6 CH$_2$ of ring), 3.36 (br.s, 1H, OH), 3.74 (m, 1H, -CH$_2$-OH). 75 MHz $^{13}$C/DEPT-135 NMR (CDCl$_3$): δ (ppm) 14.08 (+ve, terminal CH$_3$), 22.65-35.01 (-ve, CH$_2$ chain and C-3, C-4, C-5 of ring), 54.60 (-ve, C-2 and C-6 of ring), 64.91 (-ve, -CH$_2$N), 66.03 (+ve, -CH-OH). IR (CHCl$_3$) cm$^{-1}$: 3453, 2924, 1462, 1308, 1122, 879, 782, 723. MS m/z (parent ions): 326.36 and 327.36 (M$^+$+1 and M$^+$+2).

1-Morpholinododecan-2-ol (9). Viscous brown; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.88-0.93 (t, 3H, terminal CH$_3$), 1.29-1.47 (m, 18H, chain CH$_2$ and CH$_2$ α to CH-OH), 2.32-2.52 (m, 5H, -CH$_2$H$_5$N and 2, 6 CH$_2$ of ring), 2.72-2.99 (m, 2H, -CH$_2$H$_8$N and OH), 3.74-3.84 (m, 5H, -CH-OH and 3, 5 CH$_2$ of ring). 75 MHz $^{13}$C/DEPT-135 NMR (CDCl$_3$): δ (ppm) 14.33 (+ve, terminal CH$_3$), 23.17-35.30 (-ve, CH$_2$ chain), 54.03 (-ve, C-2 and C-6 of ring), 65.37 (-ve, -CH$_2$N), 66.16 (+ve, -CH-OH), 67.61 (-ve, C-3 and C-5 of ring). IR (CHCl$_3$) cm$^{-1}$: 3450, 2927, 1461, 1308, 1045, 878, 781. MS m/z (parent ions): 270.29 and 272.27 (M$^+$-1 and M$^+$+1).

1-Morpholinotetradecan-2-ol (10). White solid; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.88-0.92 (t, 3H, terminal CH$_3$), 1.28-1.46 (m, 22H, chain CH$_2$ and CH$_2$ α to CH-OH), 2.29-2.49 (m, 4H, -CH$_2$H$_5$N, -CH$_2$H$_8$N and 2 CH$_2$ of ring), 2.71-2.76 (m, 2H, 6 CH$_2$ of ring), 3.53 (br.s, 1H, OH), 3.73-3.82 (m, 5H, -CH-OH and 3, 5 CH$_2$ of ring). 75 MHz $^{13}$C/DEPT-135 NMR (CDCl$_3$): δ (ppm) 14.42 (+ve, terminal CH$_3$), 23.00-35.17 (-ve, CH$_2$ chain), 53.99 (-ve, C-2 and C-6 of ring), 65.12 (-ve, -CH$_2$N), 66.28 (+ve, -CH-OH), 67.36 (-ve, C-3 and C-5 of ring). IR (CHCl$_3$) cm$^{-1}$: 3466, 2924, 1458, 1296, 1120, 868, 637. MS m/z (parent ions): 300.30 (M$^+$+1).

1-Morpholinohexadecan-2-ol (11). White solid; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH$_3$), 1.25 (m, 24H, chain CH$_2$), 1.35-1.46 (m, 2H, CH$_2$ α to CH-OH), 2.25-2.28 (m, 1H, -CH$_2$H$_5$N), 2.32-2.39 (m, 3H, -CH$_2$H$_8$N and 2 CH$_2$ of ring), 2.62-2.67 (m, 2H, 6 CH$_2$ of ring), 3.64 (br.s, 1H, OH), 3.66-3.75 (m, 5H, -CH-OH and 3, 5
CH₂ of ring). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.10 (+ve, terminal CH₃), 22.67-34.84 (-ve, CH₂ chain), 53.65 (-ve, C-2 and C-6 of ring), 64.79 (-ve, -CH₂-N), 65.94 (+ve, -CH-OH), 67.01 (-ve, C-3 and C-5 of ring). IR (CHCl₃) cm⁻¹: 3471, 2926, 1458, 1296, 1121, 868, 795, 723. MS m/z (parent ions): 328.33 (M⁺+1).

1-(2-Hydroxydodecyl)-1-(2-hydroxyethyl)piperidin-1-ium bromide (13). Viscous yellow; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.85-0.90 (t, 3H, terminal CH₃), 1.25-1.58 (br.s, 18H, chain CH₂ and CH₂ α to CH-OH), 1.75-1.96 (m, 6H, 3, 4, 5 CH₂ of ring), 3.36-3.41 (m, 1H, C₁₀H₂₁-CH(OH)CH₃H₅-N⁺), 3.52-3.75 (m, 3H, C₁₀H₂₁-CH(OH)CH₃H₅-N⁺ and -HOCH₂CH₂-N⁺), 3.90-3.93 (m, 4H, HOCH₂CH₂-N⁺ and OH), 4.02-4.15 (m, 4H, 2, 6 CH₂ of ring), 4.31 (br.s, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.04 (+ve, terminal CH₃), 20.07-36.14 (-ve, CH₂ chain and C-3, C-4, C-5 of ring), 55.64 (-ve, C-2 and C-6 of ring), 60.94 (-ve, HOCH₂CH₂-N⁺), 61.92 (-ve, HOCH₂CH₂-N⁺), 63.76 (-ve, C₁₀H₂₁-CH(OH)CH₂-N⁺), 65.08 (+ve, -CH-OH). IR (CHCl₃) cm⁻¹: 3453, 2932, 1471, 1320, 1124, 870, 782, 735. MS positive ions m/z (for C₁₉H₄₀NO₂⁺): 314.33 and 315.11 [(M-Br)⁺ and (M-Br)⁺+1].

1-(2-Hydroxyethyl)-1-(2-hydroxytetradecyl)piperidin-1-ium bromide (14). White paste; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH₃), 1.25-1.29 (br.s, 20H, chain CH₂), 1.35-1.59 (m, 2H, CH₂ α to CH-OH), 1.75-1.96 (m, 6H, 3, 4, 5 CH₂ of ring), 3.39-3.42 (m, 1H, C₁₂H₂₅-CH(OH)CH₃H₅-N⁺), 3.66-3.77 (m, 4H, C₁₂H₂₅-CH(OH)CH₃H₅-N⁺, -HOCH₂CH₂-N⁺ and OH), 3.86-4.06 (m, 3H, HOCH₂CH₂-N⁺ and OH), 4.12-4.28 (m, 5H, -CH-OH and 2, 6 CH₂ of ring). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.08 (+ve, terminal CH₃), 20.13-36.18 (-ve, CH₂ chain and C-3, C-4, C-5 of ring), 55.67 (-ve, C-2 and C-6 of ring), 61.01 (-ve, HOCH₂CH₂-N⁺), 61.78-61.94 (-ve, HOCH₂CH₂-N⁺), 63.93 (-ve, C₁₂H₂₅-CH(OH)CH₂-N⁺), 65.10 (+ve, -CH-OH). IR (CHCl₃) cm⁻¹: 3452, 2927, 1463, 1310, 1125, 870, 783, 730. MS positive ions m/z (for C₂₁H₄₄NO₂⁺): 342.33 and 343.11 [(M-Br)⁺ and (M-Br)⁺+1].

1-(2-Hydroxyethyl)-1-(2-hydroxyhexadecyl)piperidin-1-ium bromide (15). White solid; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.85-0.90 (t, 3H, terminal CH₃), 1.25 (br.s, 24H, chain CH₂), 1.43 (m, 2H, CH₂ α to CH-OH), 1.75-1.96 (m, 6H, 3, 4, 5 CH₂ of ring), 2.70 (br.s, 2H, OH), 3.35-3.39 (m, 1H, C₁₄H₂₉-CH(OH)CH₃H₅-N⁺), 3.74 (m, 5H, C₁₄H₂₉-CH(OH)CH₃H₅-N⁺, HOCH₂CH₂-N⁺ and HOCH₂CH₂-N⁺), 3.91-4.07 (m, 4H, 2, 6 CH₂ of ring), 4.33 (br.s, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.67
(−ve, terminal CH3), 20.69-36.75 (−ve, CH2 chain and C-3, C-4, C-5 of ring), 56.28 (−ve, C-2 and C-6 of ring), 61.56 (−ve, HOCH2CH2-N+), 62.56 (−ve, HOCH2CH2-N+), 64.31 (−ve, C14H29-CH(OH)CH2-N+), 65.65 (+ve, -CH-OH). IR (CHCl3) cm⁻¹: 3450, 2927, 1461, 1307, 1114, 1046, 876, 779, 728. MS positive ions m/z (for C23H46NO2⁺): 370.32 and 371.21 [(M-Br)⁺ and (M-Br)+1].

4-(2-Hydroxydodecyl)-4-(2-hydroxyethyl)morpholin-4-ium bromide (16). Viscous brown; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.85-0.90 (t, 3H, terminal CH3), 1.25 (br.s, 16H, chain CH2), 1.49-1.60 (m, 2H, CH2 α to CH-OH), 3.01-3.05 (br.s, 2H, OH), 3.12-3.17 (m, 1H, C10H21-CH(OH)CH₃Hb-N+), 3.47-3.73 (m, 5H, C10H21-CH(OH)CH₃Hb-N+ and 3, 5 CH2 of ring), 3.89-4.10 (m, 8H, HOCH2CH2-N+, HOCH2CH2-N+ and 2, 6 CH2 of ring), 4.30-4.33 (m, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.27 (+ve, terminal CH3), 22.83-36.15 (−ve, CH2 chain), 55.87 (−ve, C-2 and C-6 of ring), 60.42 (−ve, C-3 and C-5 of ring), 60.89-61.22 (−ve, HOCH2CH2-N+ and HOCH2CH2-N+), 63.82 (−ve, C10H21-CH(OH)CH₂-N+), 65.34 (+ve, -CH-OH). IR (CHCl₃) cm⁻¹: 3467, 2926, 1456, 1293, 1125, 860, 657. MS positive ions m/z (for C18H38NO2⁺): 316.32 and 317.18 [(M-Br)⁺ and (M-Br)+1].

4-(2-Hydroxyethyl)-4-(2-hydroxytetradecyl)morpholin-4-ium bromide (17). White solid; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.85-0.90 (t, 3H, terminal CH3), 1.25-1.49 (br.s, 22H, chain CH2 and CH2 α to CH-OH), 3.10 (br.s, 2H, OH), 3.38-3.51 (m, 1H, C12H25-CH(OH)CH₃Hb-N+), 3.67-3.80 (m, 5H, C12H25-CH(OH)CH₃Hb-N+ and 3, 5 CH2 of ring), 3.93-4.09 (m, 8H, HOCH2CH2-N+, HOCH2CH2-N+ and 2, 6 CH2 of ring), 4.23 (m, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.14 (+ve, terminal CH3), 22.70-35.97 (−ve, CH2 chain), 55.70 (−ve, C-2 and C-6 of ring), 60.37 (−ve, C-3 and C-5 of ring), 60.71-61.33 (−ve, HOCH2CH2-N+ and HOCH2CH2-N+), 64.55 (−ve, C12H25-CH(OH)CH₂-N+), 65.30 (+ve, -CH-OH). IR (CHCl₃) cm⁻¹: 3455, 2920, 1455, 1312, 1050, 870, 780. MS positive ions m/z (for C20H₄₂NO₂⁺): 344.32 and 345.11[(M-Br)⁺ and (M-Br)+1].

4-(2-Hydroxyethyl)-4-(2-hydroxyhexadecyl)morpholin-4-ium bromide (18). White solid; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH3), 1.25-1.37 (br.s, 22H, chain CH2), 1.48-1.57 (m, 2H, CH2 α to CH-OH), 2.77 (br.s, 2H, OH), 3.50-3.53 (m, 1H, C14H29-CH(OH)CH₃Hb-N+), 3.68-3.87 (m, 5H, C14H29-CH(OH)CH₃Hb-N+ and 3, 5 CH2 of ring), 3.97-4.15 (m, 8H, HOCH2CH2-N+, HOCH2CH2-N+ and 2, 6 CH2 of ring), 4.28 (m, 1H, -CH-OH). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.07 (+ve, terminal
CH₃), 22.65-35.93 (-ve, CH₂ chain), 55.60 (-ve, C-2 and C-6 of ring), 60.19 (-ve, C-3 and C-5 of ring), 60.65-60.95 (-ve, HOCH₂CH₂-N⁺), 61.47 (-ve, HOCH₂CH₂-N⁺), 64.91 (-ve, C₁₄H₂₀-CH(OH)CH₂-N⁺), 65.16 (+ve, -CH-OH). **IR (CHCl₃) cm⁻¹:** 3470, 2923, 1452, 1302, 1130, 875, 790, 734. **MS positive ions m/z (for C₂₂H₄₆NO₃⁺):** 372.32 and 373.21 [(M-Br)⁺ and (M-Br)⁺+1].
Section-5.2.2: Evaluation of surface properties of Piperidinium and Morpholinium based Surfactants.

Result and discussion:

a) Self-Aggregation Studies in aqueous solution: The surface activity of the aqueous solutions was measured by surface tension measurements. Figure 5.2.7 depicts the surface tension (γ) versus log of surfactant concentration (C) plots for six piperidinium and morpholinium ILs surfactants at 25 °C. The surface tension progressively decreases with increase in concentration of surfactants and then reaches a plateau region, above which a merely constant value (γcmc) is obtained.

Values of γcmc for piperidinium ILs 13, 14 and 15 were observed as 32.06, 33.04, 33.25 mN/m while, for morpholinium ILs 16, 17 and 18 as 35.82, 37.66, 34.20 mN/m, respectively. The slight differences in γcmc values for both series can be attributed to the nature of headgroup. The trend of increase in surface tension attained at cmc for both series of surfactants can be explained on the basis of cmc/c20 ratio observed for these surfactants. The affinity of a particular surfactant to reduce surface tension depends upon cmc/c20 ratio, greater the observed value greater the tendency of the surfactant to reduce surface tension of the system.1 Further table 5.3 shows that cmc/c20 values decreases with elongation of alkyl chain length in both series, and consequently the affinity to reduce surface tension decreases with elongation of alkyl chain length with an exception in case of surfactant 18.

Further, when piperidinium and morpholinium surfactants of homologous series are compared, the surfactants bearing piperidinium headgroups (i.e 13, 14, 15) have more ability while surfactants with morpholinium headgroups (i.e 16, 17, 18) have lesser ability to reduce surface tension of aqueous system. As results demonstrated that γcmc value becomes smaller for piperidinium surfactants as compared with morpholinium surfactants of homologous series, so piperidinium surfactants have greater tendency to be adsorbed at the air-water interface than morpholinium surfactants. Above results illustrate that the effect of alkyl chain length and head group size on the γcmc are quite different.

Another important parameter, Πcmc is the surface pressure at the cmc, being defined by equation 5.2.1

\[ \Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \]  

(5.2.1)
Where $\gamma_o$ is the surface tension of pure solvent and $\gamma_{\text{cmc}}$ is the surface tension of the solution at the cmc. This parameter measures the effect of surfactant on the surface tension of pure solvent i.e water.\textsuperscript{117} The $\Pi_{\text{cmc}}$ values for studied ILs are higher than conventional cationic surfactants\textsuperscript{116}, therefore they have greater ability to reduce the tension of aqueous system. Higher $\Pi_{\text{cmc}}$ values for surfactants, 13 and 18 indicates that these ionic liquids are more effective than other surface active ILs in the reduction of surface tension.

Cmc values, listed in table 5.3, decreases in both series as expected from the increase in hydrophobicity due to the increase of hydrocarbon chain length. Ionic liquid with longer hydrocarbon chains have significantly lower cmc values, which is common trend for single-tail ionic surfactants. Indeed surfactants studied in this work have low cmc values as compared to conventional ILs\textsuperscript{116} and previously reported imidazolium ILs.\textsuperscript{61,115b,123}

At identical hydrocarbon chain length, cmc values obtained for piperidinium series are smaller than those obtained for morpholinium ILs studied herein. However, both the series give lower cmc values as compared to conventional cationic surfactants, so they have higher tendency to micellize in water.

Figure 5.2.7: Surface Tension vs log C plots for piperidinium (13-15) and morpholinium (16-18) surfactants.

The maximum surface excess concentration at the air/water interface $\Gamma_{\text{max}}$, has been calculated by applying the Gibbs adsorption isotherm\textsuperscript{117} (equation 5.2.2):  

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\[
\Gamma_{\text{max}} = -\frac{1}{2.303 n R T} \left( \frac{d \gamma}{d \log C} \right)_T \tag{5.2.2}
\]

Where \( R \) is the gas constant \( (8.314 \text{ J/molK}) \), \( T \) the absolute temperature, \( \gamma \) the surface tension, \( C \) the surfactant concentration. The value of \( n \) is taken 2 as there is one counter ion associated with one ionic head group.

The minimum area occupied per surfactant molecule \( (A_{\text{min}}) \) at the air-water interface\(^{117} \) has been obtained by using the equation \( 5.2.3 \)

\[
A_{\text{min}} = \frac{1}{N} \Gamma_{\text{max}} \tag{5.2.3}
\]

Where \( N \) is Avogadro’s number and \( A_{\text{min}} \) is in nm\(^2 \) (Table 5.3). All the surfactants \( (13-18) \) synthesised in present work have been found to be having lower \( A_{\text{min}} \) values as compared to previously reported imidazolium ionic liquids\(^{61,115b,123} \). A greater value of \( \Gamma_{\text{max}} \) and a smaller value of \( A_{\text{min}} \) means a denser arrangement of surfactant molecules at the surface of the solution\(^{91b,93} \). It is clearly seen from Table 5.3 that piperidinium ILs has a significantly large \( \Gamma_{\text{max}} \) value and a correspondingly smaller \( A_{\text{min}} \) value than morpholinium ILs, indicating a denser arrangement of piperidinium ILs molecules at the air-water interface compared with morpholinium ILs. The difference between \( A_{\text{min}} \) values in both series, suggests that variations of slopes are essentially due to the nature of head group. It is well establish that the hydrophilic head group size is a dominant factor affecting the \( \Gamma_{\text{max}} \) and \( A_{\text{min}} \) values of surfactants\(^{94} \).

The values of \( \Gamma_{\text{max}} \) have been obtained as 2.24, 2.26, 2.49, 2.24, 2.70 and 3.53 \( \mu \text{mol/m}^2 \) for 13, 14, 15, 16, 17 and 18 respectively. In regard to the available data for typical ionic surfactants\(^{116a} \), these values are closer to that for (tetradecyl)trimethylammonium bromide \( (\Gamma_{\text{max}} = 2.7 \mu \text{mol/m}^2) \) and large than that for (tetradecyl)tripropylammonium bromide \( (\Gamma_{\text{max}} = 1.9 \mu \text{mol/m}^2) \) and (hexadecyl)tripropyl ammonium bromide \( (\Gamma_{\text{max}} = 1.8 \mu \text{mol/m}^2) \). The higher value of \( \Gamma_{\text{max}} \) of cationic piperidinium and morpholinium bromide could be attributed to denser arrangement of surfactant molecules at the air-water interface.

The Gibbs free energy of micellization \( (\Delta G_{\text{mic}}^\circ) \) has been calculated with the equation\(^{118} \)

\[
\Delta G_{\text{mic}}^\circ = (2 - \alpha)RT \ln X_{\text{cmc}} \tag{5.2.4}
\]
Where $X_{\text{cmc}}$ is the mole fraction at the cmc and $\alpha$ is the extent of counter ion dissociation. The negative sign have been found for micellization free energy, which indicates thermodynamically stable micelles are formed spontaneously. The results presented in Table 5.3 indicate that the driving force for micellization becomes large as $\Delta G_{\text{mic}}$ becomes more negative.

Similarly, the Gibbs free energy of adsorption ($\Delta G_{\text{ads}}$) has been calculated with equation 5.2.5

$$\Delta G_{\text{ads}} = \Delta G_{\text{mic}} - \frac{\Pi_{\text{cmc}}}{\Gamma}$$ (5.2.5)

### Table 5.3: Surface Properties of Cationic Piperidinium and Morpholinium surfactants as determined by Surface Tension, Conductivity and Fluorescence measurements:

| Surfactant | CMC<sup>a</sup> mM | CMC<sup>b</sup> mM | CMC<sup>c</sup> mM | $\beta$ | $\gamma_{\text{cmc}}$ mN/m | $\Pi_{\text{cmc}}$ mN/m | $10^4 T_{\text{mic}}$ mol/m<sup>2</sup> | $A_{\text{m}}$ nm<sup>2</sup> | $C_{20}$ x 10<sup>4</sup> | Cmc/ $C_{20}$ | $\Delta G_{\text{mic}}$ KJ/mol | $\Delta G_{\text{ads}}$ KJ/mol |
|------------|---------------------|---------------------|---------------------|-------|--------------------------|--------------------------|-------------------------------|-----------------|-----------------|----------------|-----------------|----------------|----------------|
| 13         | 2.45                | 4.02                | 3.54                | 0.71  | 32.06                    | 40.34                    | 2.24                          | 0.74            | 3.80            | 6.4            | -40.38          | -58.38          |
| 14         | 1.69                | 2.53                | 2.18                | 0.70  | 33.04                    | 39.36                    | 2.26                          | 0.73            | 3.31            | 5.1            | -42.09          | -59.48          |
| 15         | 0.24                | 0.59                | 0.53                | 0.68  | 33.25                    | 39.15                    | 2.49                          | 0.66            | 0.52            | 4.6            | -47.66          | -63.34          |
| 16         | 2.75                | 4.16                | 3.98                | 0.77  | 35.82                    | 36.58                    | 2.24                          | 0.74            | 6.76            | 4.1            | -41.67          | -57.97          |
| 17         | 1.81                | 2.70                | 2.29                | 0.73  | 37.66                    | 34.74                    | 2.70                          | 0.61            | 6.16            | 2.9            | -42.55          | -55.42          |
| 18         | 0.30                | 0.68                | 0.63                | 0.67  | 34.20                    | 38.20                    | 3.53                          | 0.49            | 1.00            | 3.0            | -46.78          | -57.60          |

<sup>a</sup>Cmc from surface tension; <sup>b</sup>Cmc from conductivity; <sup>c</sup>Cmc from fluorescence; $\beta$, degree of counterion association; $\gamma_{\text{cmc}}$, the surface tension at the cmc; $\Pi_{\text{cmc}}$, maximum surface excess concentration; $A_{\text{m}}$, the area per molecule at the interface; $C_{20}$, the surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m; $\Delta G_{\text{mic}}$, Gibbs free energy of micellization; $\Delta G_{\text{ads}}$, Gibbs free energy of adsorption; Cmc/<i>C_{20}</i>, cmc from surface tension/<i>C_{20}</i>.

**b) Critical micelle concentration (cmc) and degree of counterion binding by conductivity measurements:** The cmc of these surfactants were further investigated by electrical conductivity measurement. Plot in figure 5.2.8 depicts the specific conductivity ($\kappa$) as a function of concentration (C) of surfactant solutions at 25 °C. It was observed that, for each surfactant, the results fit into two straight lines with different slopes. The break in the $\kappa$ versus C plot originates from the micellization of amphiphilic compounds, and the concentration corresponding to the break point is critical micelle concentration (cmc). The cmc values as determined by conductivity method was found to be higher than that obtained by surface tension method, however the trend of decrease in cmc values with increase in alkyl chain length remained the same (Table 5.3). Similar results were previously reported by Quagliotto et al for glucocationic surfactants. The cmc values of surfactants with
piperidinium headgroups (13-15) have been found to be lower than the compounds with morpholinium headgroups (16-18). The difference in cmc values may be attributed to the higher hydrophobicity of piperidinium series as compared to the morpholinium series, which makes piperidinium surfactants more surface active.

Figure 5.2.8: Specific conductivity vs concentration plots for piperidinium (13-15) and morpholinium (16-18) surfactants.

It can be seen in Figure 5.2.8 that the slopes of the linear region above cmc are smaller than below cmc. Conductivity below the cmc is due the sum of contributions of the free cations and anions of surfactants. Above the cmc, the rate of increase of conductivity is less because of micelle formation, as aggregates have a lower mobility than the free ions owing to their size and potential dissociation. The degree of counter ion dissociation (α) to be obtained from the ratio of slopes above and below cmc and degree of counter ion binding (β) to micelles is
equal to $1 - \alpha$. Calculated $\beta$ values have been listed in Table 5.3. The $\beta$ values found to vary from 0.68 to 0.71 for piperidinium and for morpholinium surfactants from 0.67 to 0.77. However we could not establish the role of headgroups because the $\beta$ values have been found for both series is comparable. The $\beta$ values decreased with elongation of alkyl chain.

c) **Fluorescence measurements:** The micellization for piperidinium and morpholinium surfactants were also investigated by steady-state fluorescence using the emission of pyrene. Pyrene monomer fluorescence emission is useful for monitoring the self-aggregation in aqueous solution. It is known that pyrene preferentially dissolves into hydrophobic regions. The emission spectra of pyrene present five vibration bands; the first band may be enhanced in a polar microenvironment, while the third band is not sensitive to the surrounding environment. Thus, the ratio of the intensity of the first to the third band ($I_1/I_3$) may not only probe the micropolarity of the surfactant aggregates, but is also used to obtain the cmc of the surfactants in aqueous solution.\(^\text{122}\) When surfactant self-assembly takes place, pyrene molecules will penetrate into the interior hydrophobic region of micelles from water.

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**Figure 5.2.9:** Ratio of the first and third vibronic bands of pyrene, $I_1/I_3$, vs log C.

Figure 5.2.9 represents the cmc values determined from the fluorescence plot shown in table 5.3 are 3.54, 2.18, 0.53 for piperidinium (13, 14, 15) and 3.98, 2.29, 0.63, for morpholinium surfactants (16, 17, 18) respectively, which are in accordance with those obtained from conductivity measurements. The surfactants with piperidinium head groups were observed to be having lower cmc values as compared to those with morpholinium head group containing surfactants by fluorescence studies also.

\(^{124}\) Lianos, P.; Lang, J. *J. Colloid Interface Sci.* **1983**, *96*, 222 - 228.
Experimental:

Surface tension measurements: Critical micelle concentration (cmc) and Surface tension attained at cmc was determined using a CSC Du Nouy interfacial tensiometer (Central scientific Co., Inc, USA) using platinum-iridium ring (circumference 5.992 cm) at 25.0 ± 0.1°C. The tensiometer was calibrated using triple distilled water. The surfactant solution was aged for 12 hours prior to the determination of surface activity. For the determination of cmc, an adequate quantity of a concentrated surfactant solution was added into 20 ml of water in order to change the surfactant concentration from concentrations well below the critical micelle concentration (cmc) to at least 2-3 times the cmc.

Conductivity measurements: Conductivity was measured on an Equip-Tronics auto temperature conductivity meter model EQ661 equipped with a conductivity cell. The solutions were thermostated in the cell at 25.0 ± 0.1 °C. For the determination of cmc, an adequate quantity of a concentrated surfactant solution was added into 25 ml of water in order to change the surfactant concentration from concentrations well below the critical micelle concentration (cmc) to at least 2-3 times the cmc. Degree of counterion binding ($\beta$) has been calculated as $(1-\alpha)$, where $\alpha = S_{\text{micellar}}/S_{\text{premicellar}}$ (i.e., ratio of the slope after and before cmc).

Fluorescence measurements: The fluorescence measurements were carried out using a PerkinElmer LS-55 spectrofluorometer at 25.0 ± 0.1 °C. Pyrene was used as the fluorescence probe. The emission spectra of pyrene was recorded from 350-500 nm after excitation at 335 nm with the slit widths fixed at 4.5 and 2.5 nm for the emission and the excitation, respectively. For the determination of cmc, an adequate quantity of a concentrated surfactant solution was added into 3 ml of pyrene solution. The ratio of the intensities of the first and third vibronic peaks ($I_1/I_3$) was used to estimate the micropolarity sensed by pyrene as well as to obtain the cmc of the surfactants.
**Section-5.2.3: Evaluation of thermal stability of Piperidinium and Morpholinium based Surfactants by thermogravimetry analysis.**

**Result and discussion:**

All the surfactants synthesised in the present study exhibited medium thermal stabilities. Most of the surfactants decomposed in a temperature range of 233 °C to 260 °C (the onset temperature). Figure 5.2.10 (a) shows a characteristic curve for the decomposition of the morpholinium surfactants 16 as measured by thermal gravimetric analyzer. The onset temperature ($T_{onset}$) is the intersection of baseline weight, either from the start of the experiment and the tangent of the weight vs temperature curve as decomposition occurs. The start temperature ($T_{start}$) is the temperature at which the decomposition of the sample begins. The onset and start temperatures for present piperidinium (13-15) and morpholinium (16-18) surfactants are listed in Table 5.4.

![Thermal decomposition curves](image)

**Figure 5.2.10:** (a) Thermal decomposition curve of surfactant 16 determined by TGA, indicating the ($T_{start}$) and ($T_{onset}$) temperature. (b) Thermal decomposition curves of surfactant 15 and 18 indicating that surfactant 15 with piperidinium headgroup of homologous series have higher thermal stability.

Thermal stability of these surfactants increases with elongation of chain length; results are in accordance with recently reported long chain $\beta$-hydroxyl-$\gamma$-alkyloxy-$N$-methyl imidazolium surfactants. Furthermore, Fig. 5.2.10 (b) shows that the thermal stability of the piperidinium surfactants slightly higher than the morpholinium surfactants. Though the ether group caused
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a negative effect to the thermal stability of ILs and the thermal decomposition temperature decreased with the increasing number of ether groups in cations.\textsuperscript{125}

Table 5.4: Onset and Start Temperatures for Thermal Decomposition of Piperidinium and Morpholinium Surfactants.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surfactant 13</th>
<th>Surfactant 14</th>
<th>Surfactant 15</th>
<th>Surfactant 16</th>
<th>Surfactant 17</th>
<th>Surfactant 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{onset}}$</td>
<td>256.6</td>
<td>249.8</td>
<td>258.6</td>
<td>233.3</td>
<td>241.1</td>
<td>243.0</td>
</tr>
<tr>
<td>$T_{\text{start}}$</td>
<td>244.0</td>
<td>233.3</td>
<td>242.0</td>
<td>211.1</td>
<td>221.6</td>
<td>212.9</td>
</tr>
</tbody>
</table>

Experimental:

Thermal stability measurements: The thermal stability of the piperidinium and morpholinium surfactants was measured with SDT Q600 Thermal Gravimetric Analyzer (TGA), using a nitrogen atmosphere. Thermograms were recorded using a heating rate of 5 °C per minute from 25 to 400 °C. The experiments were carried on alumina sample pan by using nitrogen flow rate of 100 ml per minute. Thermal stability of piperidinium and morpholinium surfactants was determined from TGA graph.