Chapter 5


Section-5.1: Synthesis, Characterization and Surface Properties of Cationic Imidazolium Surfactants.

Section-5.1.1: Synthesis and Characterization of cationic imidazolium surfactants.

Section-5.1.2: Evaluation of Surface properties of cationic imidazolium surfactants.

Section-5.1.3: Evaluation of Thermal stability of imidazolium surfactants by thermogravimetry analysis.
**Introduction:**

Cationic surfactants have attracted the attention of chemists for a long time, owing to their general synthesis and their countless applications in various fields. Currently, these surfactants are customarily used as fabric softeners, wetting agents, dispersants, emulsifiers, foaming agents, and bactericides. Recently, the use of cationic surfactants/amphiphiles in high technology areas such as soft templates for the synthesis of mesoporous materials, corrosion inhibitors, capping agent for the synthesis of nanoparticles and nanorods, biomedical applications including gene delivery and drug delivery, and antimicrobial activity has witnessed increased attention.

Cationic surfactants are a vital category of compounds having one or more hydrophobic groups attached directly or indirectly to positively charged nitrogen atoms. In the past decade, quaternary ammonium surfactants have been synthesized and studied extensively. Recently, several new categories of cationics like pyridinium, imidazolium, piperidinium, pyrrolidinium, and pyrrolium compounds have been developed and investigated.

We in the present thesis report several heterocyclic imidazolium, piperidinium and morpholinium surfactants, synthesized starting from long chain epoxides based on the principles of green chemistry. These surfactants have been investigated for their surface properties by surface tension, conductivity and fluorescence method. The thermal properties of these surfactants have also been determined by thermogravimetry analysis (TGA).

---

**Section-5.1.1: Synthesis and characterization of cationic imidazolium surfactants.**

**Result and discussion:**

Six new imidazolium surfactants have been synthesized by regioselective nucleophilic epoxy ring opening reaction by using zinc perchlorate as catalyst. 1,2-Epoxydodecane (1), 1,2-Epoxytetradecane (2) and 1,2-Epoxyhexadecane (3) on reaction with imidazole gave the respective β-hydroxy N-alkyl imidazoles (5-7). The β-hydroxy N-alkyl imidazole (5-7) thus obtained on reaction with 2-bromo ethanol (8) and 2-chloro ethanol (9) gave the respective imidazolium surfactants (Scheme – 5.1).

The structure of cationic imidazolium surfactants 10a, 10b, 11a, 11b, 12a and 12b 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 5.1.1) terminal methyl protons of the alkyl chain of all imidazolium surfactants appeared as triplet between δ 0.84-0.90 ppm. The heterocyclic protons –NCHN$^+$- and –NCHCHN$^+$- were observed between δ 9.21-9.35 ppm and δ 7.30-7.57 ppm, respectively. The methylene protons of carbon (i.e, -N-CH$_2$CH(OH)-), directly
attached to heteroatom (nitrogen) adjacent to carbon attached to hydroxy group are non-equivalent in nature and were observed as a pair of multiplets at \( \delta \) 3.94-4.15 ppm (H_a) and \( \delta \) 4.06-4.38 ppm (H_b) respectively. The signal for protons attached to C-atom bearing the hydroxyl group (i.e \( \text{CH-OH} \) and \( \text{–NCH}_2\text{CH}_2\text{-OH} \)) appeared as multiplets between \( \delta \) 3.45-3.95 ppm. The methylene protons of carbon directly attached to positively charged nitrogen atom (i.e, \( \text{N}^+\text{-CH}_2\text{CH}_2\text{OH} \)) were observed as multiplets between \( \delta \) 4.21-4.41 ppm for all these cationic imidazolium surfactants.

![Figure 5.1.1: \(^1\text{H}\) spectra of 3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1\text{H}-imidazol-3-ium bromide (12a).](image)

\(^{13}\text{C}\) NMR spectra (Figure 5.1.2) depicted \( \text{sp}^3 \) carbon for terminal methyl of the alkyl chain at \( \delta \) 14.00-14.16 ppm. The signal for carbon (i.e, \( \text{N}^+\text{-CH}_2\text{CH}_2\text{OH} \)), directly attached to the heterocyclic positively charged imidazolium nitrogen was observed at \( \delta \) 52.32-52.92 ppm. The \( \text{sp}^2 \) hybridised carbon (i.e, \( \text{-N-CH}_2\text{CH(OH)}\text{-} \)), directly attached to heteroatom (nitrogen) was observed in the range of \( \delta \) 55.62-56.22 ppm. This particular carbon (i.e., \( \text{-N-CH}_2\text{CH(OH)}\text{-} \)) was identified on the bases of DEPT spectra (Figure 5.1.3) of the molecule which appeared as negative signal in the spectra. Carbon attached to hydroxyl groups (i.e \( \text{-CH-OH} \) and \( \text{–NCH}_2\text{CH}_2\text{-OH} \)) were observed between \( \delta \) 59.85-60.00 ppm and \( \delta \) 69.15-69.40 ppm, respectively. The carbons of imidazolium ring \( \text{–NCHCHN}^+\text{-} \) were observed between \( \delta \)
122.44-122.82 ppm and \(\text{–NCHN}^+\) observed at \(\delta\) 136.47-137.03 ppm. These imidazolium ring carbons (i.e., \(-\text{NCHCHN}^+\) and \(-\text{NCHN}^+\)) in DEPT spectra appeared as positive signals.

Figure 5.1.2: \(^{13}\text{C}\) spectra of 3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1H-imidazol-3-ium bromide (12a).

Figure 5.1.3: \(^{13}\text{C}/\text{DEPT-135}\) spectra of 3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1H-imidazol-3-ium bromide (12a).
The assignment of signals in $^1$H and $^{13}$C/DEPT-135 NMR spectra as discussed is based on the $^1$H-$^{13}$C 2D HETCOR (Figure 5.1.4) and $^1$H-$^1$H 2D COSY NMR (Figure 5.1.5) spectra of these imidazolium surfactants. It can be clearly seen from the $^1$H-$^{13}$C 2D HETCOR NMR spectra of imidazolium surfactant 12a that $-\text{NCH}_2\text{N}^+$- proton of positively charged imidazolium ring is strongly deshielded and is attached to carbon at δ 136.66 (-N-CH-N$^+$-).

The methylene protons of carbon directly attached to nitrogen of imidazolium ring adjacent to carbon attached to hydroxy group (i.e. $-\text{NCH}_2\text{H}_6\text{CH(OH)}$-), observed at δ 55.84) are non-equivalent in nature and each protons gives two independent signal. Similarly, the signal for methylene protons directly attached to positively charged nitrogen of imidazolium ring (i.e. $-\text{NCH}_2\text{CH}_2\text{OH}$, observed at δ 52.56 in $^{13}$C spectra) were found to give an independent signal as broad singlet in case of imidazolium surfactant 12a integrating for two protons.

Figure 5.1.4: 2D HETCOR ($^1$H-$^{13}$C) spectra of 3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1H-imidazol-3-ium bromide (12a).

The $^1$H-$^1$H 2D COSY NMR spectra of imidazolium surfactant 12a further provided comprehensive information about the structure of imidazolium surfactant which enabled us to solve the complicated structure with much ease. In the $^1$H-$^1$H COSY spectrum the methine proton attached to hydroxyl group (i.e., $-\text{CH-OH}$) of imidazolium surfactant 12a at δ 3.93
ppm has been observed to be coupled with four protons. These protons are pairs of non-equivalent methylene protons attached to carbon directly attached to nitrogen of imidazolium ring and methylene protons adjacent to methine proton of alkyl chain length as evident from 2D HETCOR spectra of the same molecule. It is evident from 2D COSY spectrum that this methine proton is also strongly coupled with hydroxyl proton. Due to this coupling the hydroxyl proton appear as doublet at a chemical shift of δ 4.76-4.82 ppm. The same has also been confirmed by $^{13}$C-$^1$H HETCOR spectrum of imidazolium surfactant (Figure 5.1.4). Because of the presence of traces of moisture in sample due to hygroscopic nature of the amphiphilic molecule, the water bounded hydroxylic proton couple with the methine proton on the α carbon and this secondary alcohol shows hydroxylic doublet. The methine proton expected to appear as multiplet appears as a broad singlet due to strong coupling with hydroxyl proton.

![Figure 5.1.5: 2D COSY ($^1$H-$^1$H) spectra of 3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1H-imidazol-3-ium bromide (12a).](image)

The structure elucidation of the cationic imidazolium surfactants 10a, 10b, 11a, 11b, 12a and 12b have been further supported by ESI-MS (Positive ion) mass spectroscopy. The parent ion peak (base peak) for cationic imidazolium surfactants 10a, 10b, 11a, 11b, 12a and 12b have
been observed at m/z 297.3, 297.2, 325.4, 325.4, 353.2 and 353.2, respectively. These signals account for the loss of bromide ion and chloride ion from the respective surfactants leading to formation of parent ion (M-X)+. The (M-X)+1 and (M-X)+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. Imidazole, 2-bromo ethanol and 2-chloro ethanol were purchased from Central Drug House, New Delhi, India. Millipore water was used in all experiments.

The structures of all the products were confirmed by IR, NMR and mass spectra. 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 Characterization: Synthesis of imidazolium based cationic surfactants involved two steps. First step involved a regioselective synthesis of β-hydroxy N-alkyl imidazoles (5-7) by a new economical methodology. 1,2-Epoxydodecane (1), 1,2-Epoxytetradecane (2) and 1,2-Epoxyhexadecane (3) were stirred magnetically with imidazole (4) in the presence of catalytic amount of zinc perchlorate hexahydrate at 80 °C for one hour under solvent free conditions. The progress of the 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-hydroxy N-alkyl imidazoles (5-7) were purified by recrystallization in hexane and white crystalline solid separated out as a single isomer with isolated yield of 85-90%. The second step involved quaternization of β-hydroxy N-alkyl imidazoles (5-7) with 2-bromo ethanol 8 at 80 °C for 1 hour and with 2-chloro ethanol 9 quaternization were carried out at 100 °C for 5 hour (Scheme – 5.1). The resulting crude mixtures were cooled to 25 °C. The product was washed thrice with 50ml of diethyl ether and cold precipitated in acetone to get respective cationic imidazolium surfactants (10a or 10b or 11a or 11b or 12a or 12b).
1-(1H-imidazol-1-yl)dodecan-2-ol (5): White crystalline solid, mp 72-74 °C; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH$_3$), 1.26-1.37 (br. s, 16H, chain CH$_2$), 1.43-1.54 (m, 2H, CH$_2$ α to CH-OH), 3.76-3.82 (dd, 2H, -CH$_2$H$_5$-N and -CH-OH), 3.91-3.97 (dd, 1H, -CH$_2$H$_5$-N), 5.20 (br. s, 1H, OH), 6.84-6.88 (d, 2H, -NCHCHN-). 7.28-7.32 (s, 1H, -NCHN-). 75 MHz $^{13}$C/DEPT-135 NMR (CDCl$_3$): δ (ppm) 14.13 (+ve, terminal CH$_3$), 22.69-34.58 (-ve, CH$_2$ chain), 53.65 (-ve, -CH$_2$-N), 70.48 (+ve, -CH-OH), 119.71 (+ve, -NCHCHN-), 128.29 (+ve, -NCHCHN-), 137.46 (+ve, -NCHN-). IR (CHCl$_3$) cm$^{-1}$: 3408, 3230, 2919, 1563, 1459, 1350, 1237, 1108, 763. MS m/z (parent ions): 253 and 254 (M$^+$+1 and M$^+$+2).

1-(1H-imidazol-1-yl)tetradecan-2-ol (6): White crystalline solid, mp 74-75 °C; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.83-0.87 (t, 3H, terminal CH$_3$), 1.23 (br. s, 20H, chain CH$_2$), 1.45 (m, 2H, CH$_2$ α to CH-OH), 3.78-3.81 (dd, 2H, -CH$_2$H$_5$-N and -CH-OH), 3.92-3.97 (dd, 1H, -CH$_2$H$_5$-N), 5.19 (br. s, 1H, OH), 6.89-6.92 (d, 2H, -NCHCHN-), 7.39 (s, 1H, -NCHN-). 75 MHz $^{13}$C/DEPT-135 NMR (CDCl$_3$): δ (ppm) 14.05 (+ve, terminal CH$_3$), 22.62-34.52 (-ve, CH$_2$ chain), 53.55 (-ve, -CH$_2$-N), 70.51 (+ve, -CH-OH), 119.63 (+ve, -NCHCHN-), 128.35 (+ve, -NCHCHN-), 137.41 (+ve, -NCHN-). IR (CHCl$_3$) cm$^{-1}$: 3450, 3235, 2910, 1565, 1450, 1352, 1239, 1120, 750. MS m/z (parent ions): 281 and 282 (M$^+$+1 and M$^+$+2).

1-(1H-imidazol-1-yl)hexadecan-2-ol (7): White crystalline solid, mp 76-77 °C; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH$_3$), 1.25-1.35 (br. s, 24H, chain CH$_2$), 1.43-1.48 (m, 2H, CH$_2$ α to CH-OH), 3.78-3.80 (dd, 2H, -CH$_2$H$_5$-N and -CH-OH), 3.93-3.96 (dd, 1H, -CH$_2$H$_5$-N), 4.54 (br. s, 1H, OH), 6.86-6.89 (d, 2H, -NCHCHN-), 7.27-7.33 (s, 1H, -NCHN-). 75 MHz $^{13}$C/DEPT-135 NMR (CDCl$_3$): δ (ppm) 14.15 (+ve, terminal CH$_3$), 22.71-34.56 (-ve, CH$_2$ chain), 53.65 (-ve, -CH$_2$-N), 70.61 (+ve, -CH-OH), 119.68 (+ve, -NCHCHN-), 128.46 (+ve, -NCHCHN-), 137.50 (+ve, -NCHN-). IR (CHCl$_3$) cm$^{-1}$: 3420, 3230, 2915, 1570, 1455, 1347, 1245, 1126, 760. MS m/z (parent ions): 309 and 310 (M$^+$+1 and M$^+$+2).

1-(2-hydroxydodecyl)-3-(2-hydroxyethyl)-1H-imidazol-3-ium bromide (10a): White paste; 300 MHz $^1$H NMR (CDCl$_3$, TMS): δ (ppm) 0.84-0.89 (t, 3H, terminal CH$_3$), 1.24 (br. s, 16H, chain CH$_2$), 1.49 (m, 2H, CH$_2$ α to CH-OH), 3.52 (d, 2H, OH), 3.92-3.94 (m, 3H, -CH-OH and HOCH$_2$CH$_2$N$^+$), 4.06-4.14 (m, 1H, C$_{10}$H$_{21}$-CH(OH)CH$_2$H$_5$-N), 4.27-4.38 (m, 3H, C$_{10}$H$_{21}$-CH(OH)CH$_2$H$_5$-N and HOCH$_2$CH$_2$N$^+$), 7.40 (s, 1H, -NCHCHN$^+$), 7.56 (s, 1H, -
NCH\textsubscript{3}N\textsuperscript{+}), 9.21 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}). 75 MHz \textsuperscript{13}C/DEPT-135 NMR (CDCl\textsubscript{3}): δ (ppm) 14.00 (+ve, terminal CH\textsubscript{3}), 22.58-34.25 (-ve, CH\textsubscript{2} chain), 52.32 (-ve, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 55.62 (-ve, C\textsubscript{10}H\textsubscript{21}-CH(OH)CH\textsubscript{2}N−), 59.85 (-ve, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 69.30 (+ve, -CH-OH), 122.73 (+ve, −NCH\textsubscript{3}N\textsuperscript{+}), 136.47 (+ve, −NCH\textsubscript{3}N\textsuperscript{+}). IR (CHCl\textsubscript{3}) cm\textsuperscript{-1}: 3350, 3135, 2890, 1545, 1440, 1345, 1236, 1122, 745. MS positive ions m/z (for C\textsubscript{17}H\textsubscript{33}N\textsubscript{2}O\textsubscript{2}\textsuperscript{+}): 297.3 (Base peak) and 298.4 [(M-Br)\textsuperscript{+} and (M-Br)\textsuperscript{+}+1].

1-(2-hydroxydodecyl)-3-(2-hydroxyethyl)-1H-imidazol-3-ium chloride (10b): White paste; 300 MHz \textsuperscript{1}H NMR (CDCl\textsubscript{3}, TMS): δ (ppm) 0.85-0.90 (t, 3H, terminal CH\textsubscript{3}), 1.25 (br. s, 16H, chain CH\textsubscript{2}), 1.49 (m, 2H, CH\textsubscript{2} α to CH-OH), 2.96 (br. s, 3H, H\textsubscript{2}O molecule), 3.91 (m, 3H, -CH-OH and HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 4.04-4.12 (m, 1H, C\textsubscript{10}H\textsubscript{21}-CH(OH)CH\textsubscript{2}H\textsubscript{5}-N), 4.24-4.36 (m, 3H, C\textsubscript{10}H\textsubscript{21}-CH(OH)CH\textsubscript{2}H\textsubscript{5}-N and HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 5.40 (d, 2H, OH), 7.37 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}), 7.54 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}), 9.24 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}). 75 MHz \textsuperscript{13}C/DEPT-135 NMR (CDCl\textsubscript{3}): δ (ppm) 14.11 (+ve, terminal CH\textsubscript{3}), 22.68-34.40 (-ve, CH\textsubscript{2} chain), 52.39 (-ve, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 55.69 (-ve, C\textsubscript{10}H\textsubscript{21}-CH(OH)CH\textsubscript{2}N), 60.00 (-ve, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 69.40 (+ve, -CH-OH), 122.76 (+ve, −NCH\textsubscript{3}N\textsuperscript{+}), 136.72 (+ve, −NCH\textsubscript{3}N\textsuperscript{+}). IR (CHCl\textsubscript{3}) cm\textsuperscript{-1}: 3389, 3210, 2915, 1558, 1460, 1355, 1230, 1080, 760. MS positive ions m/z (for C\textsubscript{17}H\textsubscript{33}N\textsubscript{2}O\textsubscript{2}\textsuperscript{+}): 297.2 (Base peak), 298.2 and 299.3 [(M-Cl)\textsuperscript{+}, (M-Cl)\textsuperscript{+}+1 and (M-Cl)\textsuperscript{+}+2].

3-(2-hydroxyethyl)-1-(2-hydroxytetradecyl)-1H-imidazol-3-ium bromide (11a): White paste; 300 MHz \textsuperscript{1}H NMR (CDCl\textsubscript{3}, TMS): δ (ppm) 0.84-0.88 (t, 3H, terminal CH\textsubscript{3}), 1.24 (br. s, 20H, chain CH\textsubscript{2}), 1.50 (m, 2H, CH\textsubscript{2} α to CH-OH), 2.36 (br. s, 1H, H\textsubscript{2}O molecule), 3.45 (m, 3H, -CH-OH and HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 3.94 (m, 1H, C\textsubscript{12}H\textsubscript{25}-CH(OH)CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{5}-N), 4.06-4.14 (m, 1H, C\textsubscript{12}H\textsubscript{25}-CH(OH)CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{5}-N), 4.26-4.38 (m, 2H, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 4.77 (d, 2H, OH), 7.36 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}), 7.50 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}), 9.27 (s, 1H, −NCH\textsubscript{3}N\textsuperscript{+}). 75 MHz \textsuperscript{13}C/DEPT-135 NMR (CDCl\textsubscript{3}): δ (ppm) 14.03 (+ve, terminal CH\textsubscript{3}), 22.61-34.30 (-ve, CH\textsubscript{2} chain), 52.40 (-ve, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 55.69 (-ve, C\textsubscript{12}H\textsubscript{25}-CH(OH)CH\textsubscript{3}N), 59.87 (-ve, HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 69.29 (+ve, -CH-OH), 122.75 (+ve, −NCH\textsubscript{3}N\textsuperscript{+}), 136.56 (+ve, −NCH\textsubscript{3}N\textsuperscript{+}). IR (CHCl\textsubscript{3}) cm\textsuperscript{-1}: 3390, 3255, 2876, 1585, 1455, 1347, 1245, 1125, 778. MS positive ions m/z (for C\textsubscript{19}H\textsubscript{39}N\textsubscript{2}O\textsubscript{2}\textsuperscript{+}): 325.4 (Base peak), 326.4 and 327.4 [(M-Br)\textsuperscript{+}, (M-Br)\textsuperscript{+}+1 and (M-Br)\textsuperscript{+}+2].

3-(2-hydroxyethyl)-1-(2-hydroxytetradecyl)-1H-imidazol-3-ium chloride (11b): White paste; 300 MHz \textsuperscript{1}H NMR (CDCl\textsubscript{3}, TMS): δ (ppm) 0.86-0.90 (t, 3H, terminal CH\textsubscript{3}), 1.25 (br. s, 20H, chain CH\textsubscript{2}), 1.51 (m, 2H, CH\textsubscript{2} α to CH-OH), 2.45 (br. s, 2H, H\textsubscript{2}O molecule), 3.93 (m, 3H, -CH-OH and HOCH\textsubscript{2}CH\textsubscript{2}N\textsuperscript{+}), 4.05-4.13 (m, 1H, C\textsubscript{12}H\textsubscript{25}-CH(OH)CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{5}-N), 4.24-4.28
3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1H-imidazol-3-ium bromide (12a): White solid; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH₃), 1.25 (br. s, 24H, chain CH₂), 1.51 (m, 2H, CH₂ α to CH-OH), 2.93 (br. s, 1H, H₂O molecule), 3.93 (m, 3H, -CH-OH and HOCH₂CH₂-N⁺), 4.09-4.15 (m, 1H, C₁₂H₂₉-CH(OH)CH₄H₆-N), 4.29-4.32 (m, 1H, C₁₄H₂₉-CH(OH)CH₄H₆-N), 4.39-4.40 (m, 2H, HOCH₂CH₂-N⁺), 4.76-4.82 (d, 2H, OH), 7.42 (s, 1H, -NCHCHN⁺), 7.57 (s, 1H, -NCHCHN⁺), 9.26 (s, 1H, -NCHN⁺). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.15 (+ve, terminal CH₃), 22.71-34.33 (-ve, CH₂ chain), 52.56 (-ve, HOCH₂CH₂-N⁺), 55.84 (-ve, C₁₄H₂₉-CH(OH)CH₄N), 59.90 (-ve, HOCH₂CH₂-N⁺), 69.30 (+ve, -CH-OH), 122.76-122.82 (+ve, -NCHCHN⁺), 136.66 (+ve, -NCHN⁺). IR (CHCl₃) cm⁻¹: 3430, 3237, 2900, 1585, 1470, 1330, 1237, 1122, 771. MS positive ions m/z (for C₂₁H₄¹N₂O₂⁺): 353.2 (Base peak), 354.3 and 355.3 [(M-Br)+, (M-Br)+1 and (M-Br)+2].

3-(2-hydroxyethyl)-1-(2-hydroxyhexadecyl)-1H-imidazol-3-ium chloride (12b): White solid; 300 MHz ¹H NMR (CDCl₃, TMS): δ (ppm) 0.86-0.89 (t, 3H, terminal CH₃), 1.25-1.33 (br. s, 24H, chain CH₂), 1.48-1.51 (m, 2H, CH₂ α to CH-OH), 2.05-2.08 (br. s, 2H, H₂O molecule), 3.94-3.97 (m, 3H, -CH-OH and HOCH₂CH₂-N⁺), 4.05-4.11 (m, 1H, C₁₂H₂₉-CH(OH)CH₄H₆-N), 4.22-4.26 (m, 1H, C₁₄H₂₉-CH(OH)CH₄H₆-N), 4.28-4.40 (m, 2H, HOCH₂CH₂-N⁺), 5.44-5.50 (d, 2H, OH), 7.34 (s, 1H, -NCHCHN⁺), 7.48 (s, 1H, -NCHCHN⁺), 9.23 (s, 1H, -NCHN⁺). 75 MHz ¹³C/DEPT-135 NMR (CDCl₃): δ (ppm) 14.16 (+ve, terminal CH₃), 22.72-31.95 (-ve, CH₂ chain), 52.92 (-ve, HOCH₂CH₂-N⁺), 56.22 (-ve, C₁₄H₂₉-CH(OH)CH₂N), 59.89 (-ve, HOCH₂CH₂-N⁺), 69.15 (+ve, -CH-OH), 122.44-122.62 (+ve, -NCHCHN⁺), 137.03 (+ve, -NCHN⁺). IR (CHCl₃) cm⁻¹: 3380, 3215, 2885, 1570, 1466, 1342, 1250, 1124, 787. MS positive ions m/z (for C₂₁H₄¹N₂O₂⁺): 353.2 (Base peak), 354.3 and 355.2 [(M-Cl)+, (M-Cl)+1 and (M-Cl)+2].
**Section-5.1.2: Evaluation of surface properties of cationic imidazolium surfactants.**

**Result and discussion:**

**a) Self-Aggregation Studies in aqueous solution:** The surface tension was measured to evaluate the surface activity of the aqueous surfactant solutions. Figure 5.1.6 depicts the surface tension (γ) versus log of concentration (C) plots for six imidazolium surfactants at 25 °C. The surface tension decreases initially with increasing concentration of surfactants and then reaches a plateau region, indicating that micelles are formed and the concentration of break point corresponds to the critical micelle concentration.

The cmc values of these surfactants decreases with elongation of alkyl chain length. The cmc of these imidazolium surfactants (10a, 10b, 11a, 11b, 12a and 12b) have been found to be lower as compared to earlier reported imidazolium ILs.\(^{67,115}\) and as well as other cationic surfactants.\(^{116}\)

The values of \(\gamma_{\text{cmc}}\) were found to be 28.33, 31.26, 31.40, 36.03, 36.85, and 37.38 mN/m for 10a, 10b, 11a, 11b, 12a and 12b respectively. The trend of increase in surface tension attained at cmc for series of imidazolium surfactant can be explained on the basis of cmc/c\(^20\) ratio observed for these surfactants. The affinity of a particular surfactant to reduce surface tension depends upon cmc/c\(^20\) ratio, greater the observed value greater the tendency of the surfactant to reduce surface tension of the system.\(^1\) Further table 5.1 shows that cmc/c\(^20\) values decrease with elongation of alkyl chain length, with an exception of surfactant 12b and consequently the affinity to reduce surface tension decreases with increase in hydrophobic alkyl chain length. Furthermore, imidazolium surfactant 10a and 10b have maximum ability while surfactants 12a and 12b have minimum ability to reduce surface tension of aqueous system in the series of imidazolium surfactants being reported.

Further when bromo derivative and chloro derivatives of homologous series are compared, [Br\(^-\)] would be more effective than [Cl\(^-\)] for the screening of the electrostatic repulsion between the polar head groups, since [Br\(^-\)] is less hydrated than [Cl\(^-\)]. The results


demonstrated that $\gamma_{\text{cmc}}$ value becomes smaller for bromo derivative as compared to chloro derivative of homologous series, so bromo derivatives have greater tendency to adsorb at the air-water interface than chloro derivatives. Above results illustrate that the effect of alkyl chain length and counter ion species on the $\gamma_{\text{cmc}}$ are quite different.

Another important parameter, $\Pi_{\text{cmc}}$ is the surface pressure at the cmc, being defined by equation 5.1.1

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}}$$ (5.1.1)

Where $\gamma_0$ 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. Imidazolium surfactants synthesised in present work have been found to have greater ability to reduce the tension of aqueous system compared to previously reported imidazolium ILs. Higher $\Pi_{\text{cmc}}$ values for imidazolium surfactants, 10a and 10b indicates that these ionic liquids are more effective than other surface active ILs in the reduction of surface tension.

**Figure 5.1.6: Surface Tension vs log C plot for the imidazolium surfactants.**

The maximum surface excess concentration at the air/water interface $\Gamma_{\text{max}}$, has been calculated by applying the Gibbs adsorption isotherm$^{117}$ (equation 5.1.2):

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \left( \frac{d\gamma}{d \log C} \right)_T$$ (5.1.2)

---

Where \( R \) is the gas constant (8.314 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 5.1.3

\[
A_{\text{min}} = 1/N \Gamma_{\text{max}} \quad (5.1.3)
\]

Where \( N \) is Avogadro’s number and \( A_{\text{min}} \) is in nm\(^2\) (Table 5.1). All imidazolium surfactants have been found to possess lower \( A_{\text{min}} \) values as compared to previously reported imidazolium ionic liquids\(^{67,115}\). The lower \( A_{\text{min}} \) values of imidazolium surfactants 12a and 12b can be attributed to tighter packing of the longer hydrophobic chains at the interface\(^{91b,93}\). A theoretical explanation suggested that the dominant factor responsible for the variation in \( A_{\text{min}} \) values of the surfactants is size of the hydrophilic headgroup and solvation of the imidazolium cation in water\(^{94}\).

The values of \( \Gamma_{\text{max}} \) are 2.13, 2.10, 2.68, 3.88, 4.04, 3.02 \( \mu \text{mol/m}^2 \) for 10a, 10b, 11a, 11b, 12a and 12b, respectively. With reference to available data for typical cationic surfactants\(^{116a}\) these values are large to those 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 bromide could be attributed to weak hydration of its counter ion \([\text{Br}]^-\), which causes more screening effect and consequently 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 following equation\(^{118}\)

\[
\Delta G_{\text{mic}}^\circ = (2 - \alpha)RT \ln X_{\text{cmc}} \quad (5.1.4)
\]

Where \( X_{\text{cmc}} \) is the molar 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 from Table 5.1 indicate that the driving force for micellization becomes large as \( \Delta G_{\text{mic}}^\circ \) becomes more negative.

Similarly, the Gibbs free energy of adsorption ($\Delta G_{\text{ads}}^o$) has been calculated using the equation\textsuperscript{116c} 5.1.5

$$\Delta G_{\text{ads}}^o = \Delta G_{\text{mic}}^o - \frac{\pi_{\text{cmc}}}{\Gamma_{\text{max}}}$$

### TABLE 5.1: Surface Properties of Cationic imidazolium surfactants as determined by Surface Tension, Conductivity and Fluorescence measurements:

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC\textsuperscript{c} mM</th>
<th>CMC\textsuperscript{b} mM</th>
<th>CMC\textsuperscript{a} mM</th>
<th>$\beta$</th>
<th>$\gamma_{\text{cmc}}$ mN/m</th>
<th>$\Pi_{\text{cmc}}$ mmHg</th>
<th>$10^3\Gamma_{\text{max}}$ mol/m$^2$</th>
<th>$A_{\text{min}}$ nm$^2$</th>
<th>$C_{20} \times 10^4$</th>
<th>$\Delta G_{\text{mic}}^o$ KJ/mol</th>
<th>$\Delta G_{\text{ads}}^o$ KJ/mol</th>
<th>CMC\textsuperscript{a}/C\textsubscript{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>1.34</td>
<td>3.18</td>
<td>2.29</td>
<td>0.71</td>
<td>28.33</td>
<td>44.07</td>
<td>2.13</td>
<td>0.78</td>
<td>1.23</td>
<td>-41.37</td>
<td>-62.06</td>
<td>10.8</td>
</tr>
<tr>
<td>10b</td>
<td>3.01</td>
<td>4.87</td>
<td>4.26</td>
<td>0.60</td>
<td>31.26</td>
<td>41.14</td>
<td>2.10</td>
<td>0.79</td>
<td>3.98</td>
<td>-37.02</td>
<td>-56.61</td>
<td>7.5</td>
</tr>
<tr>
<td>11a</td>
<td>0.70</td>
<td>1.75</td>
<td>1.48</td>
<td>0.72</td>
<td>31.40</td>
<td>41.00</td>
<td>2.68</td>
<td>0.61</td>
<td>1.65</td>
<td>-44.16</td>
<td>-59.43</td>
<td>4.2</td>
</tr>
<tr>
<td>11b</td>
<td>2.29</td>
<td>3.26</td>
<td>3.23</td>
<td>0.64</td>
<td>36.03</td>
<td>36.37</td>
<td>3.88</td>
<td>0.42</td>
<td>9.77</td>
<td>-39.58</td>
<td>-48.95</td>
<td>2.3</td>
</tr>
<tr>
<td>12a</td>
<td>0.44</td>
<td>0.79</td>
<td>0.67</td>
<td>0.75</td>
<td>36.85</td>
<td>35.55</td>
<td>4.04</td>
<td>0.41</td>
<td>1.99</td>
<td>-48.37</td>
<td>-57.17</td>
<td>2.2</td>
</tr>
<tr>
<td>12b</td>
<td>1.02</td>
<td>1.03</td>
<td>1.04</td>
<td>0.67</td>
<td>37.38</td>
<td>35.02</td>
<td>3.02</td>
<td>0.55</td>
<td>4.07</td>
<td>-45.06</td>
<td>-56.66</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Surface tension measurements; \textsuperscript{b}Electrical conductivity measurements; \textsuperscript{c}Fluorescence measurements; $\beta$, degree of counterion association; $\gamma_{\text{cmc}}$, the surface tension at the cmc; $\Gamma_{\text{max}}$, the maximum surface excess concentration; $A_{\text{min}}$, 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; $\Delta G_{\text{mic}}^o$, Gibbs free energy of micellization; $\Delta G_{\text{ads}}^o$, Gibbs free energy of adsorption; Cmc\textsuperscript{a}/C\textsubscript{20}, cmc from surface tension/C\textsubscript{20}.

**b) Critical micelle concentration (cmc) and degree of counterion binding:** We employed another technique, electrical conductivity measurements, to study the micellar aggregation behaviour of these imidazolium surfactants in aqueous solution. The specific conductivity ($\kappa$) as a function of concentration ($C$) of the surface active 1L solutions at 25 °C has been plotted in Figure 5.1.7. Each plot fits 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 of the break point corresponds to the cmc.\textsuperscript{119} The cmc values as determined by conductivity method have been found to be much higher than those obtained from surface tension measurements; however the trend of decrease in cmc values with elongation of alkyl chain length remains the same. Similar results were previously reported by Quagliotto \textit{et al}\textsuperscript{31} for glucocationic surfactants. The cmc values of surfactants with bromide counterion (10a-12a) have been found to be lower than the compounds with chloride counterion (10b-12b) while the counterion binding $\beta$ follows an opposite behaviour. Similar results have also been observed earlier by our research group for long chain $\beta$-hydroxyl-$\gamma$-alkyloxy-$N$-methylimidazolium surfactants.\textsuperscript{120} The difference in cmc values is to be attributed to the


greater electrostatic attraction of the bromide series (a) compared to the chloride series (b) because of the smaller degree of hydration of the bromide ion. This makes the hydrated chloride ion bigger than the bromide and less bound to the micelles, thus giving higher cmcs than corresponding bromide surfactants.

Figure 5.1.7: Specific conductivity vs concentration plots for the imidazolium surfactants.

c) Fluorescence method: In this study, pyrene was used as a fluorescence probe to investigate the polarity of the microenvironment of micelles. It is known that pyrene preferentially dissolves into hydrophobic regions. The emission spectra of pyrene give 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. When surfactant self-assembly takes place, pyrene molecules will penetrate into the interior hydrophobic region of micelles from water. This will cause an abrupt change of the I$_1$/I$_3$ ratio and the concentration corresponding to this abrupt change is the cmc.

![Figure 5.1.8: Ratio of the first and third vibronic bands of pyrene, I$_1$/I$_3$, vs log C.](image)

The values of cmc determined from the fluorescence plot shown in Table 5.1 are 2.29, 4.26, 1.48, 3.23, 0.67 and 1.04 mmol/L for 10a, 10b, 11a, 11b, 12a and 12b respectively. Figure 5.1.8 shows that the surfactant with chloro as the counterion has higher I$_1$/I$_3$ ratio at cmc except in case of 10b as compared to surfactant with bromo as counter ion, the hydration size of counterion may be responsible for this result. As mentioned above, the electrostatic repulsion between the cationic headgroups of chloro counterion is higher than bromo counterion, which may also cause a looser arrangement in the micelle structure. As a result, water molecules may more easily penetrate the loose micelles, resulting in their higher polarity.

**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-5.1.3: Evaluation of thermal stability of imidazolium surfactants by thermogravimetry analysis.

Result and discussion:

Thermal stability measurement shows that these imidazolium surfactants are stable upto 303 °C. Figure 5.1.9 shows a characteristic curve for the decomposition of the imidazolium surfactants 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 imidazolium surfactants are listed in Table 5.2.

![Thermal decomposition curves](image-url)

Figure 5.1.9: (a) Thermal decomposition curve of 12b determined by TGA, indicating the ($T_{start}$) and ($T_{onset}$) temperature. (b) Thermal decomposition curves of 10a, 10b indicating 10a with bromo counter ion of homologous series have higher thermal stability.

Thermal stability of these surfactants decreases with elongation of chain length, just opposite trend has been reported by our research group for long chain β-hydroxyl-γ-alkyloxy-N-methyl imidazolium surfactants. Further, Fig. 5.1.9 shows that the surfactant with bromo counter ion has higher thermal stability as compare to chloro ion. The large size of anion account for increased thermal stability of respective ionic liquid.
Table 5.2: Onset and Start Temperatures for Thermal Decomposition of Imidazolium Surfactants.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>10a</th>
<th>10b</th>
<th>11a</th>
<th>11b</th>
<th>12a</th>
<th>12b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{onset}$</td>
<td>302.2</td>
<td>291.6</td>
<td>297.5</td>
<td>289.7</td>
<td>293.6</td>
<td>285.8</td>
</tr>
<tr>
<td>$T_{start}$</td>
<td>281.1</td>
<td>261.5</td>
<td>273.1</td>
<td>272.2</td>
<td>271.2</td>
<td>250.0</td>
</tr>
</tbody>
</table>

Experimental:

**Thermal stability Measurements:** The thermal stability of the imidazolium surfactants were 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 100ml per minute. Thermal stability of imidazolium surfactants was determined from TGA graph.