Summary
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The requirement of 21st century is to synthesize important industrial chemicals directly from renewable feed stock as well as using a green approach. Fats and oils are renewable feed stock that can be treated chemically or enzymatically to derive materials which often act as a replacement for petroleum-derived materials. One of the useful reaction for the modification of oleochemicals is epoxidation and it serve as a valuable chemical intermediate, transformable to a wide variety of products i.e amino alcohols and surfactants.

Keeping these facts in view, we planned the present work with the following objectives.

1. To synthesize new long chain amino alcohols and cationic Surfactants from renewable as well as petrochemical raw materials using epoxides as intermediates by cost effective and energy saving methodology.
2. To characterize the structure of these new molecules by several available spectroscopic techniques.
3. To evaluate surface properties of cationic amphiphiles by using techniques like surface tension, conductivity and fluorescence method.
4. To study interaction of cationic surfactants with DNA and evaluate their cytotoxicity.
5. To measure thermal stability of cationic surfactants.

The work done to achieve the above objectives has been organized in two parts in the thesis.

Part 1 of the work deals with the synthesis and characterisation of long chain β-amino alcohols by epoxy ring-opening reactions of epoxy fatty acid methyl ester.

Part II describes the synthesis and evaluation of new cationic surfactants using the epoxy ring opening reactions.

Part - I

Chapter 1:

Section 1.1 is the brief introduction of the work embodied in this thesis.

In Section 1.2 the literature related to the synthesis of 1,2-amino alcohols has been reviewed briefly.
Chapter 2:

Section 2.1: Synthesis of β-Amino Alcohols from Internal Epoxy Fatty Acid Methyl Esters.

The internal epoxy fatty acid methyl esters, methyl 9, 10-epoxyoctadecanoate (1) under solvent free conditions react with aliphatic [butyl (2), octyl (3)], cyclic [pyrrolidine (4), piperidine (5), morpholine (6)] and aromatic [p-chloro aniline (7), p-anisidine (8), benzyl amine (9) and aniline (10)] amines in the presence of catalyst zinc (II) perchlorate hexahydrate to give an isomeric mixture of 1, 2-amino alcohols [11a(b)-19a(b)] in a yield ranging from 65 to 85 percent (Scheme - 2.1). The structures of all these new β-amino alcohols were confirmed by IR, NMR and Mass spectroscopy.

\[
\begin{align*}
\text{R} & = \text{C}_4\text{H}_9\text{H}_5 (2), \text{C}_6\text{H}_4\text{H}_9\text{H}_5 (3), \text{C}_6\text{H}_5\text{H}_9\text{H}_5 (4), \text{C}_6\text{H}_4\text{H}_9\text{H}_5 \text{(5)}, \text{C}_6\text{H}_4\text{H}_9\text{Cl} \text{(7)}, \text{C}_6\text{H}_4\text{H}_9\text{OCH}_3 \text{(8)}, \\
\text{R}_1 & = \text{CH}_3-\text{CH}_2\text{H}_2\text{-} , \text{R}_2 = (\text{CH}_2\text{H}_2)\text{H}_2\text{-CO}_2\text{H}_3
\end{align*}
\]

Scheme - 2.1

Section 2.2: Synthesis of β-Amino Alcohols from Terminal Epoxy Fatty Acid Methyl Ester.

The terminal epoxy fatty acid methyl esters, methyl 10, 11-epoxyundecanoate (1) under solvent free condition reacted with cyclic amines [pyrrolidine (2), piperidine (3), morpholine (4)], aliphatic amines [butyl amine (5), octyl amine (6)] and aromatic amines [p-chloro aniline (7), benzyl amine (8)] in the presence of catalyst zinc (II) perchlorate hexahydrate resulting in the formation of single isomer of 1, 2-amino alcohols (9-15) in a yield ranging from 70 to 85 percent (Scheme - 2.2). Each of the products have been characterised by IR, NMR and Mass spectroscopy.

\[
\begin{align*}
\text{R} & = \text{C}_4\text{H}_9\text{H}_5 (2), \text{C}_6\text{H}_4\text{H}_9\text{H}_5 (3), \text{C}_6\text{H}_5\text{H}_9\text{H}_5 (4), \text{C}_6\text{H}_4\text{H}_9\text{H}_5 \text{(5)}, \text{C}_6\text{H}_4\text{H}_9\text{Cl} \text{(7)}, \text{C}_6\text{H}_4\text{H}_9\text{H}_2 \text{(8)}
\end{align*}
\]

Scheme - 2.2
Part - II

Chapter 3:

Section 3.1 is the brief introduction of cationic surfactants.

In Section 3.2 the literature related to the synthesis and properties of cationic surfactants have been reviewed briefly.

Chapter 4:

*Gemini Imidazolium Surfactants: Synthesis and their Bio-Physiochemical Studies.*

**Section 4.1: Synthesis and characterization of gemini imidazolium surfactants.**

Five new heterocyclic gemini imidazolium surfactants having hydroxy group have been synthesized starting from 1,2-epoxydodecane and imidazole by energy saving and cost effective green methodology (Scheme - 4.1). Initially stoichiometric ratio of 1,2-epoxydodecane (1) and imidazole (2) were reacted in the presence of catalytic amount of zinc perchlorate to get 1-(1H-imidazol-1-yl)dodecan-2-ol (3) which were subsequently reacted with various dibromides (4-8) to get new hydroxy group containing gemini imidazolium surfactants (9-13). The structures of all these new gemini imidazolium surfactants were confirmed by elemental analysis, IR, NMR and Mass spectroscopy.

**Step 1**

\[
\text{[1]} + \text{[2]} \xrightarrow{\text{Zn (ClO}_4)_2 \cdot 6\text{H}_2\text{O, neat, 80 }^\circ\text{C, 1 hour}} \text{[3]}
\]

**Step 2**

\[
\text{[3]} + \text{[4 - 8]} \xrightarrow{\text{30 min, neat, 80 }^\circ\text{C}} \text{[9 - 13]}
\]

n = 3 for surfactant [9]; n = 4 for surfactant [10]; n = 5 for surfactant [11]; n = 6 for surfactant [12] and n = 8 for surfactant [13]

**Scheme - 4.1**

**Section 4.2: Evaluation of surface properties of gemini imidazolium surfactants.**

The surface properties of these gemini imidazolium surfactants were evaluated by surface tension and conductivity method. Their cmc values increased with increase in spacer chain length. These surfactants have low cmc values as compared to other category of gemini...
cationic surfactants and exhibit peculiarities at sufficiently low concentration as they were found to be forming premicellar aggregates in wide range of concentration below their cmc values. Krafft temperature of these gemini surfactants have been determined by conductivity method and found to be less than 25 °C.

**Section 4.3: Evaluation of thermal stability of gemini imidazolium surfactants by thermogravimetry analysis.**

Thermal stability and water of hydration of these new gemini imidazolium surfactants was determined by thermogravimetry analysis. The thermal stability of these gemini imidazolium surfactants decreases with increasing spacer length.

**Section 4.4: Evaluation of DNA binding properties of gemini imidazolium surfactants.**

These gemini imidazolium surfactants have also been evaluated for their DNA binding properties. The preliminary studies conducted by agarose gel electrophoresis indicated that all gemini imidazolium surfactants were able to bind plamid DNA at low concentration. These results have been further confirmed by ethidium bromide exclusion experiments using fluorescence spectroscopy.

**Section 4.5: Evaluation of cytotoxicity of gemini imidazolium surfactants.**

These gemini imidazolium surfactants (9-13) have been found to be less cytotoxic on C6 glioma cells (cancerous brain cell line) compared to conventional quaternary ammonium gemini surfactant 12-2-12 by MTT assay. The toxicity of these gemini surfactants increases with increasing spacer length.

**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.**

Six new imidazolium surfactants have been synthesized by regioselective nucleophilic substitution reaction by using zinc perchlorate as catalyst. 1,2-Epoxyalkanes (1-3) on reaction with imidazole gave the respective intermediates β-hydroxy N-alkyl imidazole (5-7). The intermediates were quaternized with 2-bromo ethanol (8) and 2-chloro ethanol (9) to get the imidazolium surfactants (Scheme – 5.1). The structures of these new imidazolium surfactants have been established by elemental analysis, IR, NMR and Mass spectroscopy.
Section 5.1.2: Evaluation of Surface Properties of Cationic Imidazolium Surfactants.

The surface properties of these imidazolium surfactants have been determined by surface tension, conductivity and fluorescence method. The cmc values of these surfactants decreases with increase of hydrocarbon 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 ionic liquids and as well as other cationic surfactants.

Section 5.1.3: Evaluation of Thermal stability of Cationic Imidazolium Surfactants by Thermogravimetry Analysis.

Thermal stability of these new cationic imidazolium surfactants was determined by thermogravimetry analysis. The thermal stability of these surfactants decreases with increasing alkyl chain length. The surfactant with bromo counter ion has been found to be higher thermal stability as compare to chloro ion.

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

Section 5.2.1: Synthesis and characterization of Piperidinium and Morpholinium based Cationic surfactants.
New cationic surfactants containing piperidine and morpholine headgroups have been synthesised by regioselective nucleophilic substitution reaction by using zinc perchlorate as catalyst (Scheme 5.2).

\[ \text{Step 1} \]

\[ \text{[1-3]} \] + \[ \text{[4&5]} \] \xrightarrow{\text{Zn (ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O, neat, 80 °C, 1 hour}} \[ \text{[6-11]} \]

\[ \text{Step 2} \]

\[ \text{[6-11]} \] + \[ \text{[12]} \] \xrightarrow{\text{neat, 100 °C, 10 hour}} \[ \text{[13-18]} \]

\[ n = 7 & R = \text{CH}_2 \text{ (Intermediate 6 & Surfactant 13)}\]
\[ n = 9 & R = \text{CH}_2 \text{ (Intermediate 7 & Surfactant 14)}\]
\[ n = 11 & R = \text{CH}_2 \text{ (Intermediate 8 & Surfactant 15)}\]
\[ n = 7 & R = \text{O (Intermediate 9 & Surfactant 16)}\]
\[ n = 9 & R = \text{O (Intermediate 10 & Surfactant 17)}\]
\[ n = 11 & R = \text{O (Intermediate 11 & Surfactant 18)}\]

**Scheme - 5.2**

1,2-Epoxyalkanes (1-3) on reaction with piperidine (4) and morpholine (5) gave the respective \( \beta \)-amino alcohols (6-11). The \( \beta \)-amino alcohols (6-11) thus obtained on reaction with 2-bromo ethanol gave the respective cationic surfactants (13-18). The structures of these new cationic surfactants (13-18) have been established by elemental analysis, IR, NMR and Mass spectroscopy.

**Section 5.2.2: Evaluation of Surface properties of Piperidinium and Morpholinium based Cationic surfactants.**

The surface properties of these piperidinium and morpholinium surfactants have been determined by surface tension, conductivity and fluorescence method. The cmc values of these surfactants decreases with increase of hydrocarbon chain length. For an identical hydrocarbon chain length, the cmc values obtained for piperidinium (13-15) series are smaller than those obtained for morpholinium surfactants (16-18). The cmc of these cationic surfactants (13-18) have been found to be lower as compared to earlier reported imidazolium ionic liquids and as well as other cationic surfactants.
Section 5.2.3: Evaluation of Thermal stability of Piperidinium and Morpholinium based Cationic surfactants.

Thermal stability of these new cationic piperidinium (13-15) and morpholinium (16-18) surfactants was determined by thermogravimetry analysis. The thermal stability of these cationic surfactants increases with increasing alkyl chain length. The thermal stability of the piperidinium surfactants have been found to slightly higher than morpholinium surfactants.