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Synthesis, characterization and applications of some novel cationic surfactants

Divya

Abstract
The word surfactant is a combination of three word "Surface Active Agent" that lowers the surface tension between a two liquid or between a liquid or solid. These are amphiphilic molecules containing both hydrophilic (water loving) hydrophobic part (water hating). Therefore the surfactant molecules contain both a water insoluble or oil soluble and oil insoluble and water soluble components. In general view, any material which affects the surface tension can be treated as a surfactant but in the practical view, it may act as a wetting agent, emulsifiers, foaming agents and dispersants also. The first surface active product was prepared by Scholar in Germany in 1930. The curiosity of science has formed the research work in surfactant are like organization of its molecules into some interesting shapes and structures having different and unique characteristics. This article deals with synthesis, properties and applications of new novel cationic surfactants.

Keywords: Cationic surfactants, micro emulsion, dispersing and emulsifying, properties surface tension

Introduction

Branch of chemistry known as Oleochemicals is well-founded and well-developed and some of its applications reach far back in history. During the past decade, production and utilization of oleochemicals have grown in size and diversity [1]. Thus new and interesting oleochemicals are being exploited for industrial utilization. Oleochemicals are essential to a variety of industrial products such as surfactants, plasticizers, lubricant additives, cosmetics, pharmaceuticals, soaps, detergents, textiles, plastics, protective coatings, dispersants, intermediate chemicals, urethane derivatives, organic pesticides and a variety of synthetic intermediates. In the industrial field there has been competition between oleochemicals and petrochemicals [2]. The ever increasing cost of petrochemicals and the environmental factors has diverted the attention of chemist to the synthesis of new Oleochemicals derived from natural fats and oils.

The world production of soaps, detergents and other surfactants was about 18 Mt (million tons) in 1970, 25 Mt in 1990 and 40 Mt in 2000 (not counting polymeric surfactants). Approximately 25% corresponds to the North American market and 25% to the European market. The qualitative evolution of the market in the past 50 years is very significative. In fact, in 1940 the world production of surfactants (1.6 Mt) essentially consisted of soaps (fatty acid salts) manufactured according to a very old fashioned technology. At the end of World War II, the petroleum refining market was offering short olefins, particularly C2-C3, as a by-product from catalytic cracking. In the early 1950's propylene had not yet any use, whereas ethylene started to be employed in styrene manufacturing. The low cost of propylene and the possibility of polymerizing it to produce C9-C12-C15 hydrophobic groups made it a cheap alternative to alkyl groups coming from natural or synthetic fatty acids. Synthetic detergents of the alkyl benzene sulfonate (ABS) type were born, and they soon displaced soaps for washing machine and other domestic uses.

In the early 1960's many rivers and lakes receiving the waste waters from large cities started to be covered by persistent foams, which resulted in ecological damage because the thick layer curtailed photosynthesis and oxygen dissolution. Surfactant manufacturers had to find new raw materials and methods to make linear alkylates, e.g., ethylene polymerization, molecular sieve extraction and Edelman process through the urea-paraffin complex.

In 1970's manufactures displayed a proliferation of new formulas, and a strong increase in the use of surfactants not only for domestic use but also for industrial purposes.

Novel surfactants which are now a days available for incorporation into various formulation of personal care and cosmetic product, medicine, gene therapy etc. are numerous, implying a permanent need for their classification. The overview of novel surfactant provides essential information relating to the synthesis, basic physicochemical characterstic, application and other relevant data on surfactants [1]. Surfactant properties play important roles in the performance of a wide array of industrial and consumer products [2] including detergents, paints, paper product, pharmaceuticals and cosmetics. Surfactants are also used as emulsifiers during enhanced oil recovery from deeply located oil wells [3] by increasing the apparent solubility of petroleum components and effectively reducing the interfacial tension of oil and water in situ. In modern life, it is impossible to avoid our daily products containing surfactants for instance with soap, shampoo, laundry, detergent, tooth paste as well as many pharmaceutical formulations, food product, household detergents and personal care product or indirectly in the production and processing of material which surround us [4-6]. The first surface-active product was prepared commercially by C. Scholar in Germany in 1930 [7]. Scientific curiosity has driven surfactant research into areas such as organization of surfactant molecules into interesting shapes and structures, all with unique properties [8]. The word "Surfactant" is contraction of the three words "surface active agent" that lowers the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. In the general sense, any material that affects the interfacial surface tension can be considered as a surfactant, but in the practical sense, surfactant may act as wetting agent, emulsifiers, foaming agents, and dispersants [9]. Surfactants are usually organic compounds that are amphiphilic meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their head) [10] (shown in Figure 1), therefore a surfactant contains both a water insoluble (and oil soluble) components and a water soluble component. Surfactants will defuse in water and adsorb at interface between air and water or at the interface between oil and water in the case where water mix with oil. The water insoluble hydrophobic group may extend out of the bulk water phase into air or into the oil phase, while the water soluble head group remains in the water phase.

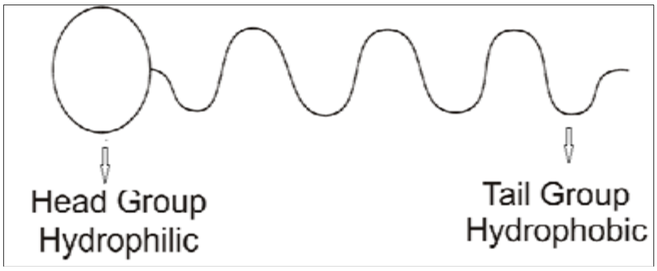


Fig 1: Schematic representation of a surfactant

In some usage surfactants are defined as molecules capable of associating to form micelles (shown in Figure 2 a, b). The following formula shows an amphiphilic molecule which is commonly used in shampoos (sodium dodecyl sulfate) (As shown in figure 3). Amphiphilicity of the surfactant molecule leads to characteristic properties i.e. adsorption (surface activity) at an interface and aggregation (self association) in a given medium. In the bulk aqueous medium or phase, surfactants form masses or aggregation such as micelles, where the hydrophobic tails from the core and the hydrophilic heads are immersed in the surrounding liquid. Other types of structure can also be formed such as spherical micelles or lipid bilayers. The shape of molecules depends on the balance in size between hydrophilic head and hydrophilic tail. A measure of this is the HLB, Hydrophilic – lipophilic balance. Higher HLB surfactants (> 10) are hydrophilic ("water loving ") and form O/W (oil in water) emulsions. Lipophilic surfactants posses low HlB values (1-10) and form W/O (water in oil) emulsions. Dish detergents, surfactants for emulsion polymerization, and the following example (SLS= sodium lauryl sulfate) are high HLB surfactants. The dynamics of surface active agent adsorption is of great importance for practical applications such as in emulsifying or coating processes as well as foaming, where bubbles or drops are rapidly generated and need to be stabilized. As the interface is created, the adsorption is limited by the diffusion of the surfactant to the interface, which can result in the kinetics being limited. These energy barriers can be due to steric or electrostatic repulsions; steric repulsions from the basis of how dispersants function. Surface rheology of surfactant layers, are important to the stability of foams and emulsions. Most surfactants "tails" are fairly similar, consisting of a hydrocarbon chain, which can be branched, linear, or aromatic. Recent advances in surfactant technology has seen the development of mixed chains or / and complex structures.

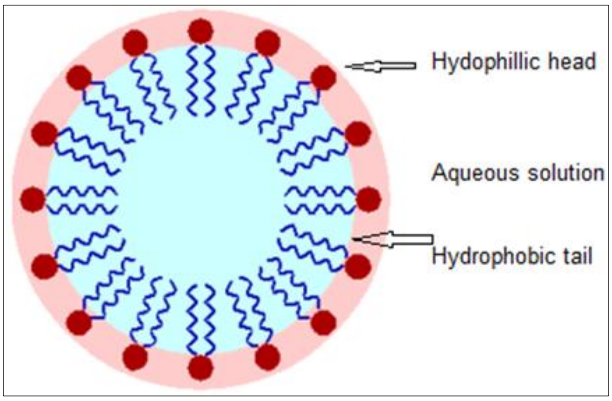


Fig 2a: Schematic diagram of a micelle of oil in aqueous suspension

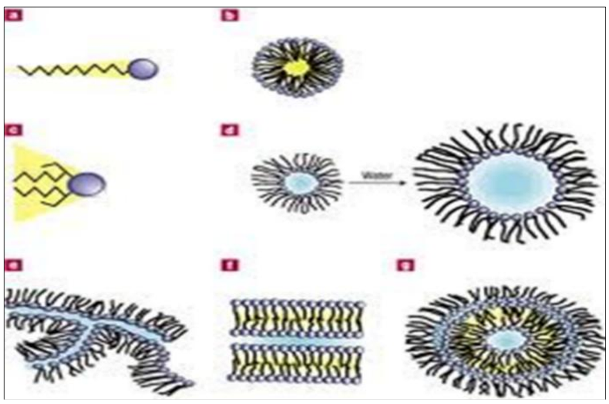


Fig 2b: Formation of reverse micelles in surfactants

World production of surfactants is estimated at 15mton/y, of which about half are soaps. Other surfactants produced on a particularly large scale are linear alkyl benzenes sulphonates (1700kton/y), lignin sulphonates (600kton/y) fatty alcohol ethoxylate (700kton/y) and alkylphenol ethoxylates (500kton/y) [11].

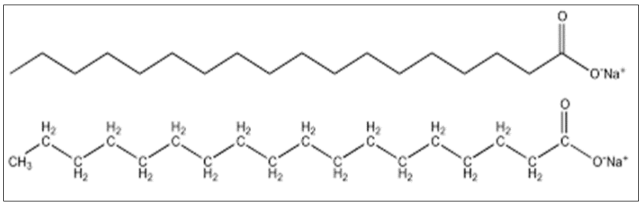


Fig 3: Sodium stearate the most common components of most soap, which comprises about 50% of commercial surfactant

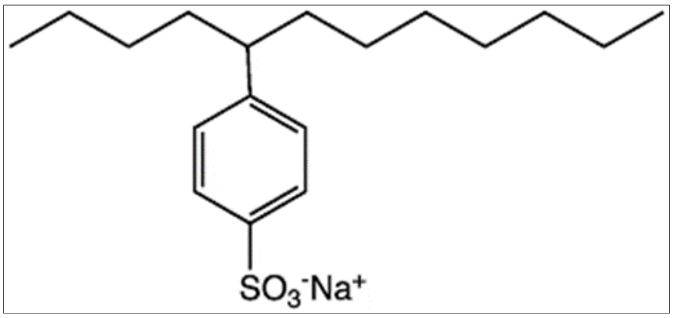


Fig 4: 4-(5-dodecyl benzene Sulfonate: A linear dodecyl benzene Sulfonate; one of the most common surfactants. Pulmonary surfactant provides a coating on the surface of the alveoli in the lungs. It acts to prevent fluid accumulation, keep airways dry, and maintain surface tension within the lungs to prevent collapse.

Types of Surfactants
1. Monomeric Surfactant
2. Dimeric Surfactant
3. Bolaform Surfactant
4. Trimeric Surfactant
5. Polymeric Surfactant
6. Diblock Copolymer

Monomeric surfactants
Conventional surfactant has a single hydrophobic tail connected to an ionic or polar head group. The head group can be negatively charged e.g. carboxylates, sulfate, sulfonate and phosphate or positively charged e.g. amine or quaternary ammonium based products.

Gemini surfactant
Gemini [12] or dimeric [13-15] surfactant are a new class of surfactant having two hydrophobic groups [15] bonded together through a linkage close to their hydrophilic group [shown in Figure 5a&5b]. The final report on Gemini surfactant like bisquaternary ammonium halide surfactant which were used to catalyze chemical reactions was given by Bunton *et al.* [12] Devin sky *et al.* [14] have reported the surface activity and micelle formation of some new " bisquaternary ammonium salt". Their surface properties were first described by Mitsui Okahara of Asaka University and his colleagues [16-20] who synthesized them in their laboratories? Menger and Littau [21] assigned the name Gemini to bis-surfactant with a rigid spacer (linkage) i.e. benzene, but the name was the extended to other bis or double tailed surfactant. Among the Gemini surfactant the cationic bis (alkyl dimethyl ammonium) alkane dibromide type with two tails and spacer separating of quaternary (linkage) nitrogen atom (represented as m – s – m where m is number of carbon atoms in alkyl chain and s is the number of carbon atom in spacer has received much attention.

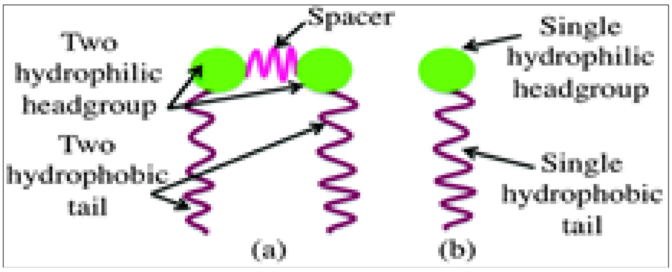


Fig 5a & 5b: Dimeric surfactant or Gemini surfactant

Bola form surfactants
Surfactants having two hydrophilic head groups connected through a hydrophobic hydrocarbon chain are called as Bolaform surfactants [shown in Figure 6a, 6b&6c]. Bola form surfactants also consist of two hydrophilic head groups connected by a long hydro carbon spacer. Their tendency for aggregation is lower and aggregation numbers are smaller than those of the corresponding monomeric surfactants.

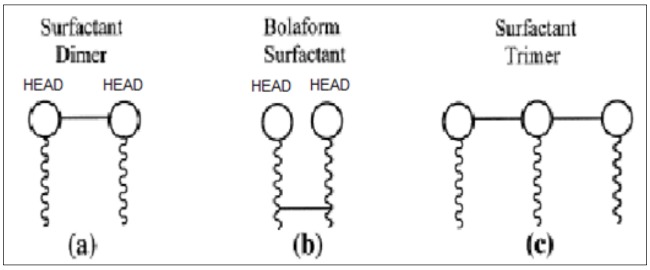


Fig 6a, 6b&6c: Bola form surfactants showing a long hydro carbon spacer

Polymeric surfactant
Polymeric surfactant is formed by the association of one or two or several macro molecular structures containing hydrophilic and lipophilic characters. It can be used as stabilizer for suspensions and emulsions recently biopolymers are also used for environment concern for example polystyrene block poly (vinyl acetate)

Classification
Surfactants are classified on the basis of their functionality or ionicity (charge) of the hydrophilic head group. (As shown in Figure 7) Surfactants are classified as:

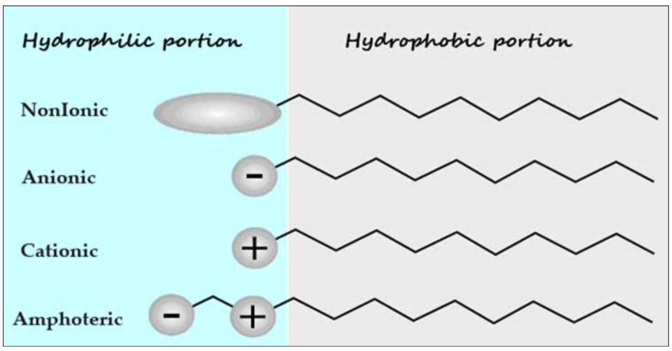


Fig 7: different types of surfactants

1. Cationic Surfactant
Cationic surfactants are comprised of a positively charged head [22]. Cationic surfactants are used as anti-microbial, antifungal; benzethonium chloride (BAC) cetylpyridinium chloride (CPC) benzethonium chloride (BZT). The cationic nature of the surfactants is not consistent with the world of non ionic and anionic charges and the disrupt cell membranes of bacteria and viruses. Example of cationic surfactant is permanently charged quaternary ammonium cation includes. Alkyl tri-methyl ammonium salts cetyl tri methyl ammonium bromide and cetyl tri methyl ammonium chloride (CTAL).

2. Anionic surfactant
Anionic surfactant contain anionic functional groups either head for e. g – sulfonate, phosphate, sulfate and carbonates, alkyl sulfates include ammonium lauryl sulfate (SLES) [shown in figure 8] [23] and sodium myreth sulfate, alkyl carboxylates (soaps) such as sodium stearate, dioctyl sodium, sulfosuccinates (DOSS), perfluoro octane sulfonates (PFOS) linear alkylbenzene sulfonates (LABS) and Perfluorobutane sulfonates alkyl aryl ether phosphates.

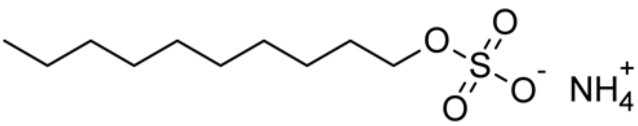


Fig 8: Ammonium lauryl sulfate

2. Zwitter ionic Surfactants or ampholytic surfactant
Zwitter ionic (amphoteric) surfactant [shown in figure 9] have both cationic and anionic centre attached to the same molecule [24]. They are those for which the charge on the polar head group can be positive or negative depending upon the PH of solution for e.g.:- Zwitter ionic surfactant is N-dodecyl-N, N-dimethyl butane. $C_{12}H_{25}N^{+}(CH_3)_2CH_2coo$- phospho lipids that constitute biomembrane are Zwitter ionic amphiphiles.

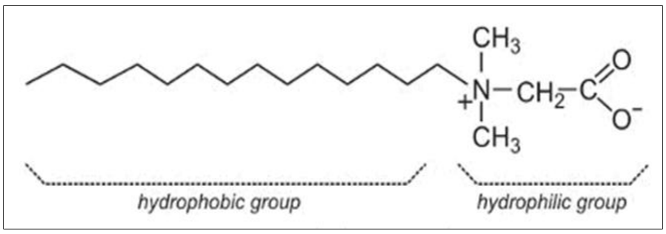


Fig 9: Zwitter ionic surfactant (an Alkyl Betaine)

3. Nonionic surfactants
The surfactants contain non ionic charge but have a polar head group containing hydroxyl groups or polyoxyethylene chains. These surfactants include multi hydroxyl product such as glycol esters, glycerol or poly glycerol esters glycosides or poly glycosides and sucrose esters. There are widely used in solubilization of insoluble organic compounds drug formulations and in cosmetics due to their low micelle concentration, less tonicity and high degradability.

Example – poly oxyethylene 20 cetyl ether (Brij 58), [shown in Figure 10] $C_{16}H_{83}$ (CH_2CH_2O)-OH1 Poly (ethylene glycol)-t-octylphenyl ether t- $C_8H_{17}C_6H_4(OCH_2CH_2)_4OH$.

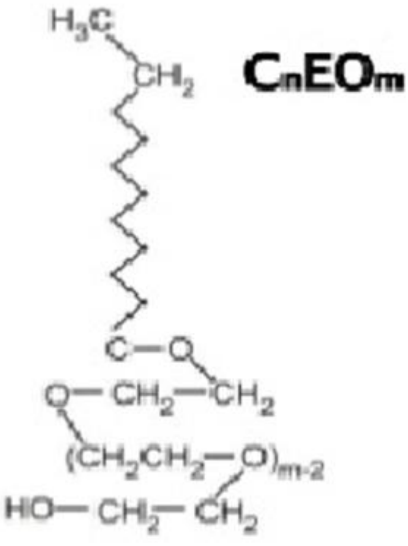
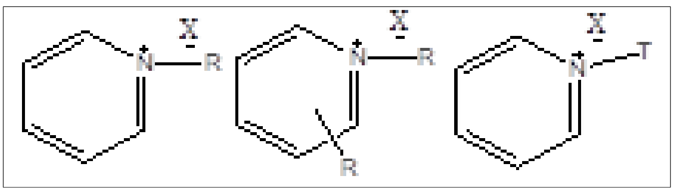


Fig 10: Alkylpolyoxyethylenes non-ionic surfactant

Review of literature
Cationic surfactants have many technical applications and used for number of stabilization problems. Cationic surfactants form strong adsorption layers and hydrophobize the surfaces of these materials are due to the predominant negatively charged nature of natural colloids and surfaces, cationic surfactant's applications include softeners, cosmetic products, electro Dicoatings and the stabilization of adhesive polymer latexes as well as in mining and paper manufacturing. In the cosmetic and detergent industries, the developments of surfactants based on natural renewable resources are the most important concept [25]. The demands for high performance surface active compounds are increasing due to the progress in industrial technology, for this demand the novel cationic Gemini surfactants have been successfully designed and developed. New class of Gemini cationic surfactants is a response to the increasing consumer demand for the products that are both greener and more efficient [26]. It is necessary to use renewable low-cast materials that are available in large quantities and to design molecular structures that show important performance favorable properties and reduced environmental impact. Various series of new surfactants have been created using environmental processes and their production permits to different products and by products of the oleo chemical industries or derived from marine resources [27], further it has been anticipated that an increased fraction of natural building blocks in the surfactant structure will be beneficial for reducing aquatic toxicity and increase the rate of biodegradation.

N-alkyl pyridinium compounds (1) are simple unsubstituted monomeric pyridinium surfactants prepared by reaction of pyridine and alkyl halide [28].



(1) (2) (3)

Where T= ester or alkoxy or benzyl

Ring substituted pyridinium surfactants (2) were prepared by the reaction of alkyl halide and ring substituted pyridine at high temperature. In N-substituted pyridinium salts (3) the nitrogen of hetrocyclic ring had been attached to various groups such as ester, alkoxy, benzyl, alkoxy methyl, acylphenethyl pyridinium chloride is pyridinium surfactant which is prepared by acylating β-phenethyl chloride by friedal craft reaction followed by reaction with pyridine to get quaternary salt. Amino pyridinium surfactants were prepared by protection of amino group of 4-amino pyridine followed by reaction with alkyl halide and alkaline hydrolysis. Pyridinium surfactants having hydrophobic alkyl chain moiety are hetrocyclic compounds and come under the category of cationic surfactants. These surfactants found countless applications in various industries and are important ingredient for several cosmetic products [29]. They are often utilized as corrosion inhibitor, in emulsion polymerization, flotation of minerals and in textile processing [30]. Biological applications of these surface active agents include their antimicrobial activity, as drug and gene delivery agent [31]. Several cationic surfactants are used in DNA extraction methods.

The last few year show an increased interest in work involving the preparation and study of surfactant based upon the natural products, some examples of surfactants are based on sugars, sterol and fatty acids. Such surfactants are interesting because they are biodegraded. A large numbers of D-gluconamides were prepared and their surface properties characterized e.g. DMSO was used as solvent [32].

A starting from the methyl ester of dehydroabietic acid, some useful N-derivatives were prepared from which several types of surfactants could potentially by synthesized, several surfactants were prepared from the acid. Chromatography or recrystallization was used for their purification.

Quagliotto [33] *et al.* recently reported new glucose based pyridinium surfactants. They refluxed α - acetobromo glucose in dry acetonitrile with 4 - (n-dodecyl) pyridine in the presence of phenol under inert conditions to get the corresponding N-(tetra –o-acetyl- -β -D-glucopyranosyl)-4-dodecylpyridinium bromide and N-(tetra-o-acetyl – -β -D-glucopyranosyl)-4-dodecyl pyridinium bromide which was then deprotected in 50% aqueous ethanol using 48% hydrobromic acid to get the 4-(n-dodecyl)-N-(α -D-glucopyranosyl) pyridinium bromide and 4-ln-dodecyl)-N-(-β -D-glucopyranosyl) pyridinium bromide.

These glucopyridinium surfactants were evaluated for their surface properties. In antimicrobial tests, these gluco-cationic surfactants showed moderate activity. Bhattacharya *et al.* [34] reported a series of novel single chain surfactants bearing one two and three pyridinium head group. The critical micellar concentrations and the degree of counterion dissociation of micelles of these surfactants were determined by conductometry. The CMC and values increased with increase in the number of head groups of the surfactants. It was found that micelle formation becomes less favourable as more head groups are increased in the surfactants.

Molecular bases of many diseases have been recognized with the development of new technology and close relationship between several fields. This led to the development of new line of treatment known as gene therapy.

Gene therapy is a modern treatment protocol for finding the defect occurring due to defective gene. This involves sending the desired encoded information with the help of some agents or vectors [35]. The agents may be viral or non-viral. Although viral vectors have shown desired results in animal models, the clinical trials on humans are still prohibited due to immunological responses which associated with the virus [36]. Gemini Cationic amphiphiles are novel delivery agents having an excellent potential for use in gene therapy. The unique property of Cationic surfactants can be seen to their greater ability to bind DNA and relatively low toxicity towards Cell line [37]. The condensed DNA and Cationic lipid complex termed as lipoplexes are readily taken up by the Cell by the process of endocytosis and are stable enough to escape endosome/lysome Compartment to pass to cytoplasm and finally to nucleus of the cell [38].

Zhou *et al.* [39] reported a series of Gemini surfactants with four methylene spacer by refluxing 1, 4- Dibromoethane and α-alkyl pyridine in ethanol for 72 hours and evaluated their surface active properties and interaction with polyacrylamide (PAM) by surface tension, fluorescence and viscosity measurements. He found that Gemini surfactants with longer hydrophobic chains have a lower CMC value, the cm of Gemini surfactants is much less than the corresponding monomeric cationic surfactants and it can form hydrophobic co-aggregates with PAM causing the pam chains to wrap up, and the viscosity of PAM also decreases. Also the longer hydrophobic chains of surfactants have stronger interactions with the PAM owing to stronger interactions with PAM

Steroid based surfactants like steroid glucosides were derived from cholesterol derivatives and Glucose. 6-O-acyl – [-β]-D-glucosyl-[-β] sitosterol isolated from ficus Carica, Moraceae was recently found to be an anti-cancer agent.

Interesting surfactant was prepared from the hydrolysis product of the natural, sugar based polymer chitosan, 2-deoxy –2-amino-D-glucose i.e. Amino glucose amides PH-based sensitive surfactant was developed from D-Fructose for example –2-Alkylamino-2-dioxy-D-glucopyranese and 1, 2-Dialkylamino-1, 2-Dideoxy D-(N)- -β -gluco pyranoside.

Some progress was made in attempts to prepare certain other natural product based surfactants for example the peppermint smelling 3-D-benzyl-L-(+)-ascorbic acid was prepared in low yield.

A number of surfactants were synthesized from sugar and natural hydrophobic compounds Monosaccharides incl. D-glucose, 2-deoxy -2-amino-D-glucose, D-fructose and D-(+)glucono-1, 5-lactone were used for the hydrophilic moiety of the surfactants. Some surfactants were found to be particularly interesting 1-deoxy-1-octyl amino –D-glucitol is a very good foaming and wetting agent as well as a good dispersion and emulsification agents. These surfactants are composed of two cationic head groups and two hydrophobic groups separated by a spacer group. These surfactants show much better surface active properties than their conventional analogs.

In addition to pyridinium cationic surfactants several imidazolium based cationic surfactants have also been synthesized. Baltazar *et al.* [40] recently reported different monocationic and Dicationic Imidazolium based amphiphiles and determined the CMC of these new series of ionic liquid type surfactants. Monocationic Imidazolium amphiphiles were synthesized by refluxing either 1-butylimidazole or 1-methylimidazole with corresponding 1-bromoalkane. Dicationic imidazolium amphiphiles were prepared by reacting imidazole and acrylonitrile in methanol to get corresponding 3-(1H-imidazol-1-yl) Propanenitrile which was then refluxed with 1-bromooctane or 1-bromododecane to get 1-(2-cyanoethyl)-3-alkyl-1H-imidazol-3-ium bromide. which was then treared with 15% aq NaOH to get 1-alkyl-1H-imidazole. The former was then quaternised with 1,2 dibromobutane and 1,2 dibromo pentane to get Gemini surfactants.

Das *et al.* [41] reported several monomeric imidazole based cationic amphiphile and evaluated their activity in the presence of interfacially active enzymes, Chromobacterium viscosum (CV) Lipase and horseradish peroxidase (HRP). It was found that enzyme activity increased with concentration of Imidazolium surfactant and also with its alkyl tail length.

El Seoud *et al.* [42] reported several monomeric imidazole based cationic amphiphiles and studied their adsorption and aggregation behaviour by surface tension measurement, conductivity, electromotive force, fluorescence quenching of micelle –solubilized pyrene, and static light scattering methods. It was found that an increase in the length of alkyl chain resulted in increase in micelle aggregation number, a decrease in minimum area/surfactant molecule at solution/air interface; critical micelle concentration and degree of counter ion dissociation.

Zheng *et al.* [43] have synthesized new long chain N-arylimidazolium ionic liquid type surfactants and their aggregation behavior has been systematically explored by florescence, surface tension, conductivity and NMR experiments. These new 1-(2,4,6-trimethylphenyl)-3-alkylimidazolium bromides have lower CMC as compared to conventional cationic bromides account for strong electrostatic self-repulsion and Π-Π interactions amoung head groups.

Zheng *et al.* reported a chiral long chain Imidazolium surfactant and the micellar behavior of this surfactant have been systematically explored by surface tension, electrical conductivity, and florescence and NMR techniques.

Sunitha *et al.* [44] synthesized aromatic ether functionalized cationic monomeric Gemini Imidazolium amphiphiles with different aliphatic chains. The surface behavior and related parameters of these mono cationic and dicationic amphiphiles have been explored by surface tension method.

Zhai *et al.* [45] have recently reported two studies of Gemini Imidazolium amphiphiles *viz*., Endo Gemini amphiphiles whose positive charges are positioned on the insides of headgroups and Exo - Gemini amphiphile in which positives charges are positioned at the two ends of the amphiphilic molecule.

On the basis of much better surface active properties and huge applications of these surfactants, we should synthesis the new type of surfactants that is cationic Gemini surfactants.

Aims and objectives of the thesis

The various synthetic methods leads to surface active compounds whose properties can be changing hydrophobic moiety or the concentration between the hydrophile and the hydrophobe. This aims or goal will provide the possibilities for the development easily degradable renewable, cheap and easily synthesized surfactant. The aims during the development of synthetic procedure have been to minimize the number of steps and provide a base for the development of industrial application. There is no universal surfactant good for every possible application. Different surfactants are needed for different applications for example for wetting and foaming. The main aims and objective of the thesis are as follow:

1. To synthesis the new type of novel cationic surfactants.
2. To find out the cost efficient procedure therefore starting material derived in bulk such as common monosaccharide, rosin acids, fatty acids etc.
3. To study Physio chemical properties of novel cationic surfactants by surface tension and conductivity.
4. To evaluate the compound for their thermal stability.
5. To investigate the various uses and application of novel surfactants.
6. To characterized ionic compound by various spectroscopy techniques such as NMR spectroscopy mass spectroscopy or infrared spectroscopy etc.
7. To understand the physical characteristics and surface properties based on the structural elements of the hydrophobe.

References

1. Milica Lukic, Ivana Pantelic Snezana Savik, an overview of novel surfactants, 2006, 7-19.
2. Svensson M. Novel surfactants, Holmberg K. (Ed), 1998, 179.
3. Shah DO. Surface Phenomena in enhanced oil recovery, Plenum Press edited by Shah, 3.
4. Rubingh DN, Holland PM. cationic surfactants – Physical Chemistry, Surfactant Science series, 1990.
5. Moroi Y. Micelles, Theoretical and applied Aspects, 1992.
6. Zana R. structure-Performance Relationship in surfactants, K. Esumi and M. Veno [Eds.], 2003.
7. Schick MJ, Nonionic surfactants MJ. Schick [Ed.], 1967.
8. Rosen MJ. Surfactant and interfacial phenomena, Wiley 3rd Ed., 2004.
9. Rosen MJ, Kunjappu JT. Surfactants and interfacial Phenomena, 2012 Hoboken, New Jersey, John Wiley & Sons, 2017.
10. Bubbles B. The lipid Chronicles, 2011, 2012.
11. Kosswig K. surfactants, Ull Mann's Encyclopedia of Industrial Chemistry Wiley – UCH, 2005.
12. Bunton CA, Robinson L, Shaak J, Stam FM, Org J. Chem., 1971, 36.
13. Ulberg Z, Podolskaya V. Zh. Kolloidn, 1978, 40.
14. Devinsky F, Lacko I, Mlynarcik D, Racansky V, Kransnce L. Tens. Det., 1985, 22.
15. Bhattacharya S, Haldar J, Langmuir, 2004, 20.
16. Okahara M, Masuyama A, Sumida Y, Zhu YP, Jpn J. Oil Chemistry Soc., 1988, 37.
17. Zhu YP, Masuyama A Okahara M. J. Am. Oil Chem. Soc., 1990, 67.
18. Zhu YP, Masuyama A, Nagata T, Okahara M, Jpn J. Oil Chem. Soc., 1991, 40.
19. Zhu YP, Masuyama A, Okahara M, Am J. Oil Chem. Soc., 1991, 68.
20. Zhu YP, Masuyama A, Kirito YL, Okahara M, Am J Oil Chem. Soc., 1991, 68.
21. Manger FM, Littau CA, Am J. Chem. Soc., 1991, 113.
22. Hirsch M. article surface active agent, 2015.
23. Hirsch M. article surface active agent, 2016.

24. Gonenne, Mofffatt, article on zwitter ionic surfactant
25. Benvegnu T, Plusquellec D, Lemiegue L, Belgacem MN, Gandini A, in Monomers, polymers and composites from renewable resources, 2008.
26. Hatanaka K, Hiryana T. Liquid cleaning cosmetic containing acidic polymers and Nitrogen hetrocyclic cationic surfactants, 1993.
27. Madaan P, Tyagi VK. General of Oleo Science, 2008, 197, 215.
28. Bunton CA, Robinson L, Schaak J, Stam MF. Journal of Organic Chemistry, 1971.
29. Richmond JM. Cationic Surfactants Science Series, 1990.
30. Free ML. Corrosion Science, 2002.
31. Lehn P, Fabrega S, Oudrhiri N. Navarro, Journal of Adv drug Delivery Reviews, 1998.
32. Peter Piispanen S. synthesis and characterization of surfactant based on natural Product, 2002.
33. Quagliotto P, Viscardi G, Barolo C, Barni E, Bellinvia S, Fisicaro E, Compari C. Journal of Organic Chemistry, 2000.
34. Bhattacharya S, Haldar Jayanta, J. Langmuir, 2005.
35. Karande P, mitragotri S. pharmaceutical, 2000, 660-665.
36. Llies MA, Seitz WA, Ghiviriga I, Johnson BH, Miller A, Thompson EB. Journal of medicinal chemistry. 2000, 3744-3754.
37. Goto M, Momota A, Ono T. journal of chemical engineering japan, 2004, 666-668.
38. Luo D, Saltzman WM. Nature Biotechnology, 2000.
39. Zhou L, Jiiang X, Chen Z, Hu X. Langmuir, 2007.
40. Baltazar Q, Chandawalla J, Sawyer K, Anderson JL. Colloids and Surfaces A: Physicochem. Eng. Aspects, 2007, 302, 150-156.
41. Das D, Biochimie PK, 2008, 820-829.
42. El Seoud, Pirse OA, Moghny PAR, Bastos TA, Journal of Colloid and Interface Science, 2007, 313, 296-304.
43. Li WX, Gao AY, Liu J, Zheng L, Chen B, Wu ZL, Tung HCJ. Colloid Interface Science, 2010, 343, 94-101.
44. Sunitha S, Reddy SP, Prasad NBR, Eue SJ. Kanjilala Lipid Science. Technol, 2011, 113, 756-762.
45. Zhai X, Liu MJ. Colloid Interface Science, 2006, 295, 181-187.