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Gemini Imidazolinium Surfactants: A Versatile Class of Molecules

Kajol Bhati, Divya Bajpai Tripathy and Anjali Gupta

Abstract

Gemini imidazolinium surfactants fascinated the researchers and many industries towards it due to their distinct molecular structure. It belongs to the cationic surfactant group. The variation in the physicochemical properties of the gemini surfactant can be achieved by changing the characteristics in the structure. There are several applications of imidazolinium such as antistatic agents, fabric softener that makes it a demanding surfactant in detergent industries as well as in the laundry industries due to the immense number of properties like dispersibility, viscosity, desirable storage stability, emulsification, critical micelle concentration and fabric conditioning etc. This book chapter discussed about the Gemini imidazolinium surfactants and its various properties, synthesis methods and applications in various fields.

Keywords: gemini, surfactants, imidazoline, imidazolinium, emulsification

1. Introduction

The use of surfactants has been increasing due to their enormous applications in the field of chemistry. They belong to the organic compound group used in oil recovery, pharmaceuticals, nanoscience, biological activity, fabric softener, antibacterial and anti-foaming agents, and other technologies [1, 2]. Gemini is categorized as a surfactant and was first used by Menger in 1990 [3]. The word gemini means dimeric, an amphiphilic molecule, earlier it used to be synthesized by joining the two discrete surfactant molecules by a rigid spacer. It contains two terminal hydrocarbon tails (short or long); two polar head groups (cationic, anionic, or nonionic); and a spacer (short or long, flexible or rigid) [4]. The gemini surfactant has an efficiency of self- assembling at low concentration. In assessment with other surfactants, the gemini surfactant shows better surface activity. The presence of two polar groups and two terminal tails also made it more hydrophobic and hydrophilic as compared to monomeric surfactant systems. The substantial qualities of gemini viz., economic efficiency, flexibility, and functionality lead to its speedy demand in the field of research as well as in industry for examination and the use of it in various products. They also have other enhanced properties like low critical micelle concentration, wetting properties, efficient for high adsorption process, low surface tension, vesicle formation, helps in reduction of interfacial tension, and have the quality for aggregation [5]. The variation in the physicochemical properties of the gemini surfactant can be achieved by changing the characteristics in the structure. The cationic gemini surfactant has a wide range of purposes in the synthesis of

nanorods, nanoparticles, construction of porous material, the formation of skincare products, drug development, gene therapy, and in antimicrobial process. Some examples of cationic gemini surfactants are piperidinium, pyridinium, imidazolium, imidazolinium, amino acid, and pyrrolidinium [6] (**Figure 1**).

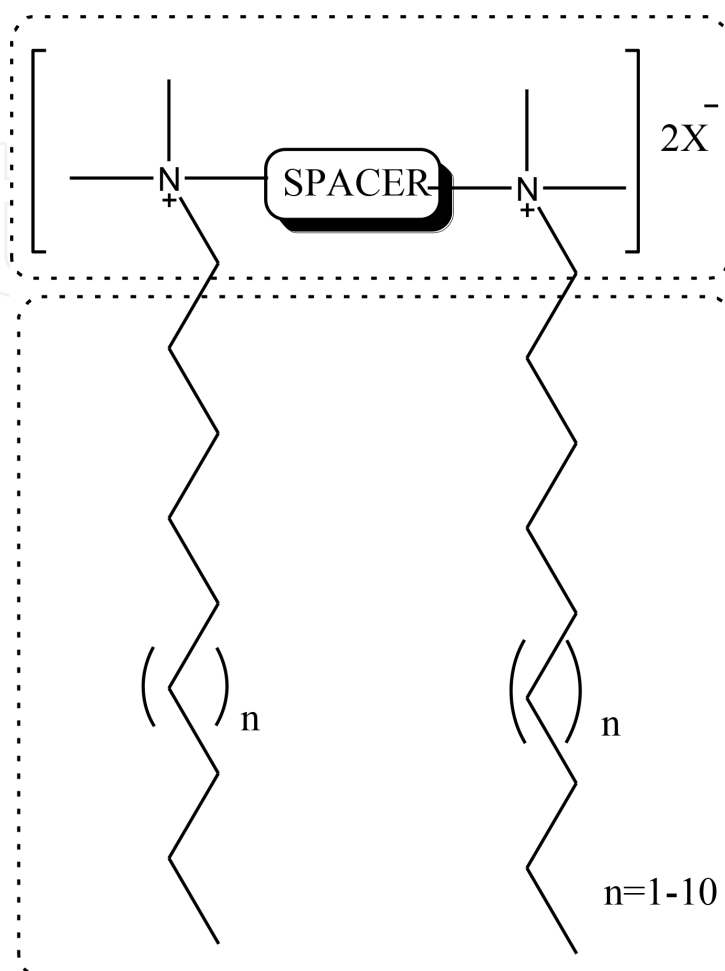


Figure 1.
Gemini surfactant [4].

As per the conducted studies, the spacer in the gemini surfactant has played a significant role in aggregation property. Examination conducted by Wanger et al. on cationic Gemini surfactants showed that spacer group has effect on the aggregation properties in aqueous solution. The use of hydrophilic compound and flexible spacer group helped in the formation of closely packed micelle structure as compared to the surfactant with rigid spacer group and hydrophobic compound. The micelle formation leads to decrease in surface tension of gemini surfactant which helps in increasing the surface area of surfactant. Therefore, use of hydrophilic compound and flexible spacer is in favorable condition for a better version of gemini surfactants. On gemini quaternary ammonium surfactants Zana et al. observed the behavior of association due to the spacer group in aqueous solution. Studies were conducted by Grosmaire et al. [7] on gemini surfactant spacer group to check the importance of carbon number on the micellization enthalpy for alkanediyl- α, ω -bis (dimethyl alkyl ammonium bromide) surfactants showed that the values of ΔH_m° were strongly dependent on the spacer carbon number. In the transmission electron microscopy, the carbon position of $\text{C}_{12}\text{-C-C}_{12}$ reflected the thread-like formation of micelle when concentration was less than 2% wt. and when the solution contained $\text{C}_{12}\text{-3-C}_{12}$ with 7% wt.; the micelles shape was elongated. To cover better surface area, the formation of micelle concentration is crucial in

surfactant as it lowers the surface tensions and hence, the minimum amount of gemini surfactant can be used in formulation process and for the applications.

1.1 Imidazolium gemini surfactant

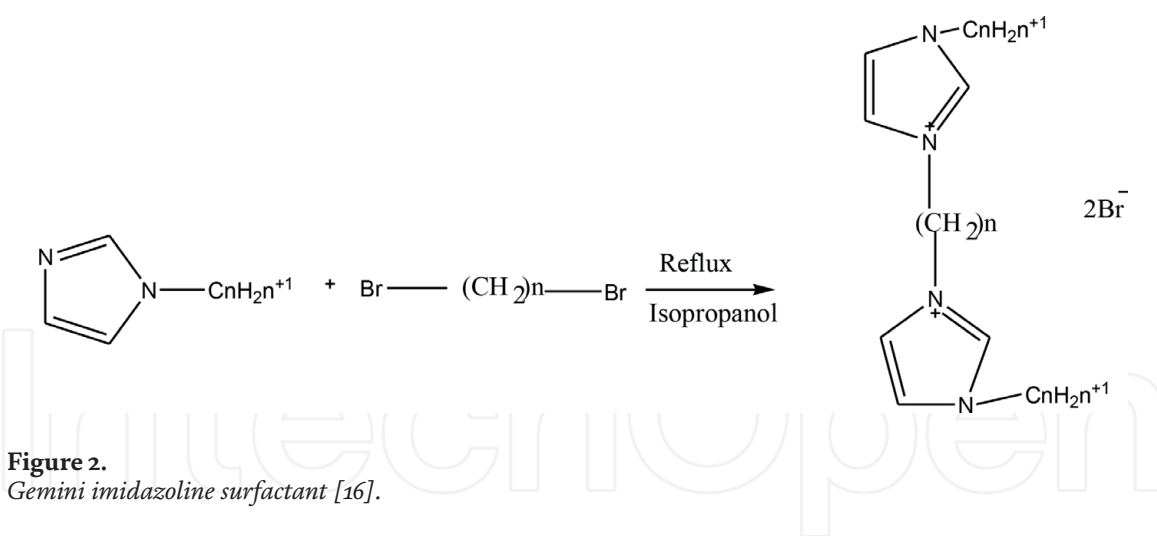
The imidazolium is one of the varieties of cationic gemini Surfactant hence named gemini Imidazolium Surfactants. The nature of imidazolium is inherent and has greater potential than any other conventional surfactant. It has a self-aggregation tendency because of the high polarization nature of its head group. Researchers are focusing on imidazolium for advanced applications and for generating an enhanced variety [8]. Studies were conducted by Bhadani et al. for the synthesis of gemini surfactants taken from cardanol oil. They synthesized two sequences of imidazolium and pyridinium based upon phenoxy ring. The hydroxyl substituted pyridinium gemini surfactants with inconstant tail length and the other sequence with a variable length of the spacer group containing hydroxyl groups in their hydrophobic carbon chains for synthesis process [9, 10]. The synthesis of the gemini surfactant with variable length of the spacer comprising hydroxyl groups in their hydrophobic carbon chains Gemini surfactant has reported by P. Patial et al. [11]. They further assessed the surface properties of the synthesized surfactants [7, 12]. This carbon chain length is useful factor in the efficiency of surfactant, shorter the length of carbon chain, higher the suppressive efficiency of gemini surfactant [13].

1.2 Imidazolinium gemini surfactants

Gemini imidazoline surfactant fascinated the researchers and many industries towards it due to their distinct molecular structure. The bonding groups involvement is the crucial aspect in gemini surfactant for the modification of structure which affects the interface and solution properties [13, 14]. Conventional imidazolinium surfactant used to form with a polar imidazolinium head group and a long hydrocarbon tails, it used to be single chain structures whereas the Gemini imidazolinium surfactants are made up of two polar imidazolinium head group and two tails of hydrocarbon in which head groups are linked by a spacer [15]. It has enhanced surface-active properties than the conventional surfactants like corrosion inhibition, dispersibility, low critical micelle concentration, and hold better qualities as a softening agent [13, 16–18]. The Gemini surfactants are formed by adding two monomer surfactants with a binding group where the length of the monomer end chain can vary in length. It can be anionic, non-anionic, or cationic whereas the binding group varies in length and can be inflexible, soft, aromatic, or aliphatic. Other distinct chemicals and physical properties of gemini imidazoline surfactants are lower kraft point, the ability of self-assembling, high density, compatibility, inimitable rheological properties, etc. It has some other applications in drug delivery, nanoscience, and nanotechnology, molecular biology, in porous constituents, biological activity, etc.

The applications of imidazolinium such as antistatic agents, fabric softener make it a demanding surfactant in detergent industries as well as the laundry industries due to the immense number of properties like dispersibility, viscosity, desirable storage stability and fabric conditioning [16] (**Figure 2**).

As per the researches, the adaptation of various methods for synthesis and designing has been adopted which leads to the variation and enhancement in the synthesis methods and a better product. Some of the researchers prepared the gemini imidazolinium surfactant by microwave synthesis process that enhanced synthesis efficiency and also studied their surface properties. The microwave synthesized the surfactant in 5–10 minutes with a better yield of 80–91% as compared to conventional method i.e. thermal condensation which produced 75–80% [19–22]. The comparative study



has also been done by Jianbin Huang on gemini and Bola, and the role of cephalic groups was found to be important as they alter their properties. A. Migahed et al. studied about the ligand length and its effect on the sustained release performance. The analysis showed that the shorter the length of the ligand, the better would be the effect of the sustained release [17]. Huaivu Yang et al. studied the relationship between sustained release and temperature and concluded that sustained release is directly proportional to the temperature [23]. A study done on emulsifier properties of gemini surfactants and applied it to emulsified asphalt and concluded that the minute quantity of gemini surfactant can be used in emulsified asphalt. Zhang Guanghua's et al. confirmed the sustained release effect on tinplate by synthesizing it. Yangjiang et al. studied the anti-corrosion properties of gemini surfactants and found that the surfactant works better during slow compound release [24]. All these studies analyzed the aspects of sustained release, surface properties, and length of the interval. Few of the methods used for synthesis helped in increasing the instability [25].

The gemini surfactants were compared with other single chain molecules, in which the gemini molecule structure was ambiguous. This was further studied to check the uniqueness and sustained release performance of gemini imidazoline surfactant. The comparison has been done between single- chain molecule and gemini imidazoline surfactant to observed the variations more precisely. The outcomes showed the great inhibitive efficiency in HCl solution as compared to single chain molecule. It also showed the better inhibitive effect on copper in HCl solution. The different concentration of gemini surfactant were taken to check the effect of concentration on inhibition property and it results that the inhibitive efficiency was higher when the concentration of HCl solution was less whereas for better inhibitive effect the concentration of gemini imidazoline surfactant must be more [25].

2. Classification

Gemini imidazoline surfactant can be classified on the basis physicochemical characteristics.

2.1 On the basis of charge

Gemini imidazolinium belongs to the cationic gemini group but they are also amphoteric in nature. The imidazolinium gemini surfactant are dimeric molecules formed by two head groups associated with the spacer group and two hydrophobic tails [26] (**Figure 3**).

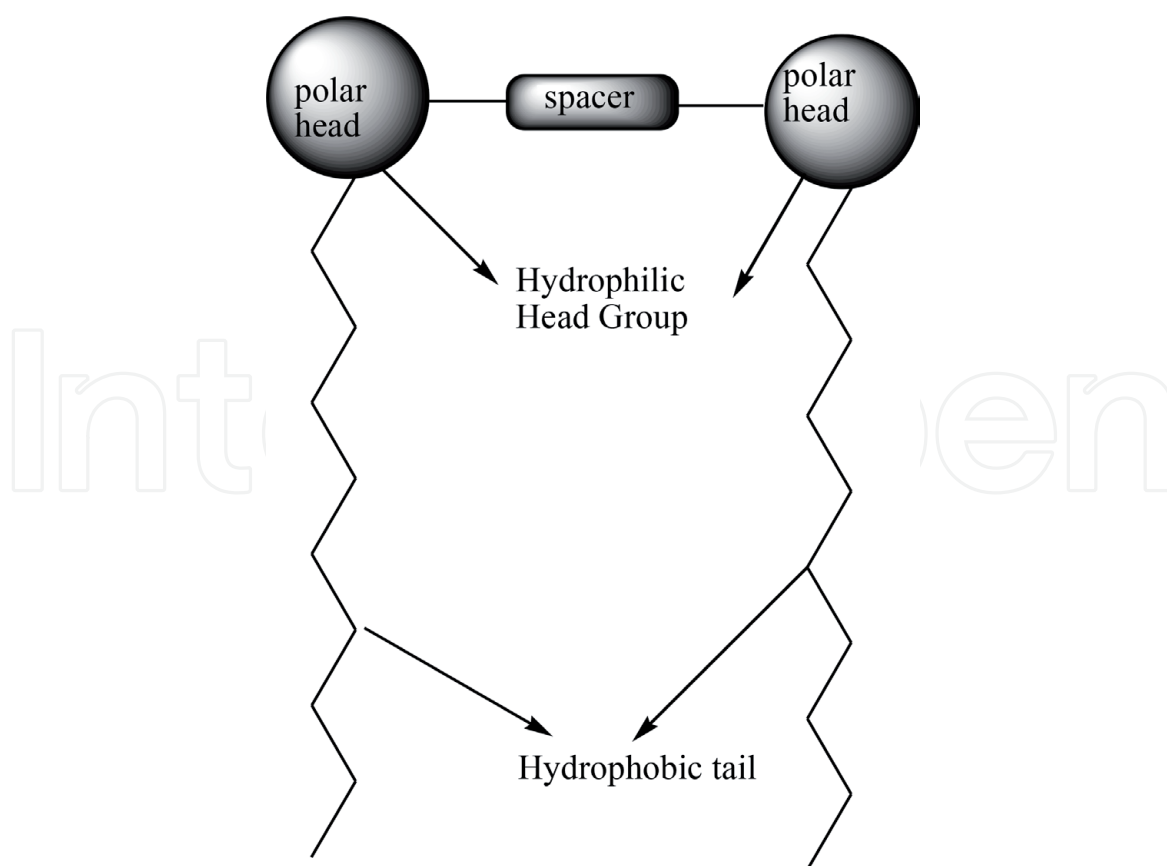


Figure 3.
Gemini imidazoline surfactant.

2.1.1 Cationic charge

The head group in the gemini imidazolinium surfactants contains the positive charge. It possesses long alkyl group, two polar imidazolinium head group and two tails of hydrocarbon in which head groups are linked by a spacer. They are soluble in organic solvents and disperse in water, eg., imidazoline-based dissymmetric bis-quaternary ammonium Gemini surfactant [26–28].

2.1.2 Amphoteric charge

The head group carries both negative and positive charge groups. They maintained the stability at acidic and basic pH of the solution, soluble in water, e.g. bisalkyl-bisimidazoline surfactant [26, 27, 29].

2.2 On the basis of spacer

The rigidity, length, polarity of the spacer can vary and leads to the variation in the structure of the gemini imidazoline surfactant as well as the in the surface properties [30, 31] (**Table 1**).

2.3 On the basis of hydrophobic tail

The variation in the hydrocarbon chain/tail can change the properties of surfactant. The chain can have two identical hydrophobic tails and two non-identical hydrophobic tails [30].

S.NO	Spacer properties	Characteristics	Sub-division
1.	Length	The surface activity of the surfactant varies with the number of carbon atoms present in the spacer group. Shorter the length of the surfactant better is the surface activity of gemini imidazoline surfactant.	<ul style="list-style-type: none">• Shorter spacer chain.• Longer spacer chain.
2.	Rigidity	Shows higher surface activity. This can effect the aggregation of surfactant.	<ul style="list-style-type: none">• Flexible spacer• Non-rigid spacer
3.	Polarity	Polarity affects the Critical micelle concentration of the surfactant	<ul style="list-style-type: none">• Polar spacer

Table 1.
Classification of gemini imidazolinium surfactant on the basis of spacer group.

3. Synthesis

3.1 Synthesis of Gemini imidazole compound

Li et al. (1997) synthesized the Gemini imidazoline by a commercial process by taking 46.7 g of triethylene tetramine hydrate (0.25 mol), 146.6 g of oleic acid (0.52 mol) and added them in toluene (100 cm³) (DIAGRAM). With continuous stirring of the solution, it was heated until it reached to the toluene boiling point (120–130 C) almost for 3 hours. After that toluene azeotrope or water was collected from the reaction and temperature has been raised to 160–170 C at 12-16th hour of reaction by simultaneous removal of toluene from the Barrett distilling receiver. Thin layer chromatography was done to check the compounds in the reaction by taking chloroform/methanol (80: 20) as solvent and spot visualized using iodine. The completion of condensation reaction was checked by the TLC plate as the spot disappearance corresponding to the monoamides and diamides resulted in its completion. The reaction further continued till 16 hours for the collection of all byproduct water and yielded 96% of product which further recrystallized for the identification and structure confirmation from chloroform [32].

The two compounds Diethylenetriamine and lauric (molar ratio of 1:1.2) mixed with the xylene, which behaved as a solvent and kept at 140°C. Zinc powder has been added as a catalyzer. The Diethylenetriamine added into the flask at a slow rate and left for the reaction for 2 hours. Later, this flask was connected with the water separator at 200°C for 8 hours. A specific volume of water has been evaporated as per the theoretical calculation after the solvent were removed using the distillation method with the temperature maintained at 140°C to obtained the imidazoline intermediate is oily in nature and yellow in color. The distillation process was performed again to obtain the Single-chain imidazoline quaternary ammonium salt. The temperature was controlled around 80–90°C for 5 hours with the addition of dimethyl- carbonate in it with the same molar quantity as imidazoline intermediate. In this product, some amount of 1,3-dibromopropane has been added as half molar volume compared to intermediate and left for 8 hours for the reactivity, resulted in a sticky liquid of red-brown. Decreased the temperature to 50°C, after that added the less quantity of acetone to it, filtrated out to extract the zinc powder. Solution kept untouched until the crystal appeared, and lifted with sucking filtration and washed with acetone for numerous times. The obtained product was the Gemini imidazolinium surfactant that is solid khaki. (LG is 1,3-di(1-methyl-1-ethylamino-2-n-undecyl-4,5-dihydro-imidazoline) propane Gemini which is the Gemini cationic imidazoline surfactants based on lauric acid and LM is

1-enthylamino-2-n-undecyl-4,5-dihydro-imidazoline which is the cationic monomeric surfactants based on lauric acid [25] (**Figure 4**).

Migahed et al. (2018) synthesized the Gemini imidazole compound by taking the 0.2 mol dicarboxylic acid (aspartic or glutamic) in 100 ml of xylene, which was further mixed with the 0.4 ml of diethylenetriamine followed by refluxed process kept for 3 hours with the addition of catalyst PTSA in 0.1% amount at 140 C. Xylene has been removed from the solution after the required amount of water (0.2 mol) was obtained in the Dean-Stark tube. The resultant product was processed with diethyl ether for required amide compounds. For next 6 hours, the temperature of the reaction has been raised to 200 C. cool down the solution when collected water reached to the desired amount to obtain the Gemini compounds [17].

He further processed the obtained Gemini compounds for the synthesis of Gemini di-quaternary ammonium compound. The 1 mol compound was refluxed with 2 mol of dodecyl chloride in ethanol for 3 days. After that, ethanol was distilled off from the solution. Di- quaternary ammonium chloride has been obtained as resultant which was washed with the diethyl ether. The characterization and structure confirmation was done by FTIR (ATI Mattson series FTIR™) revealed the functional groups of the compound [17].

3.2 Synthesis of Gemini imidazoline amphoteric surfactant

3.2.1 Synthesis of Bisalkyl-bis-imidazoline intermediate

A 250-ml four-necked flask was taken in which lauric acid with the twofold amount (in mol) and triethylenetetramine were charged and temperature maintained at 160 C for reaction under atmospheric nitrogen for 1.5 hours. Temperature has been raised to 200 C and heated for 1 hour and again raised to 250 C and heated for 1.5 hours. This process resulted in the formation of a light-yellow solid. This product further washed with ethanol, petroleum ether, and ethyl acetate (1:1:1 ratio) and resulted in bisalkyl-bisimidazoline [21] (**Figure 5**).

3.2.2 Quaternization of the Bisalkyl-bis-imidazoline intermediate

The intermediate of imidazoline was taken in a 250 ml four-necked flask and mixed with the two times the theoretical amount of sodium 2-chloroethanesulfonic acid.

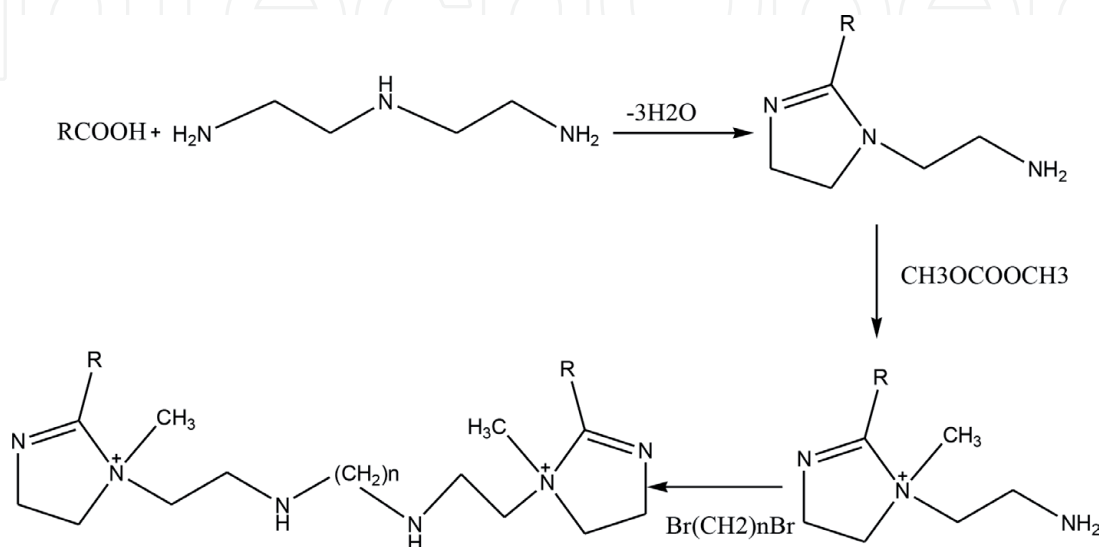


Figure 4.
 Synthesis of LG [25].

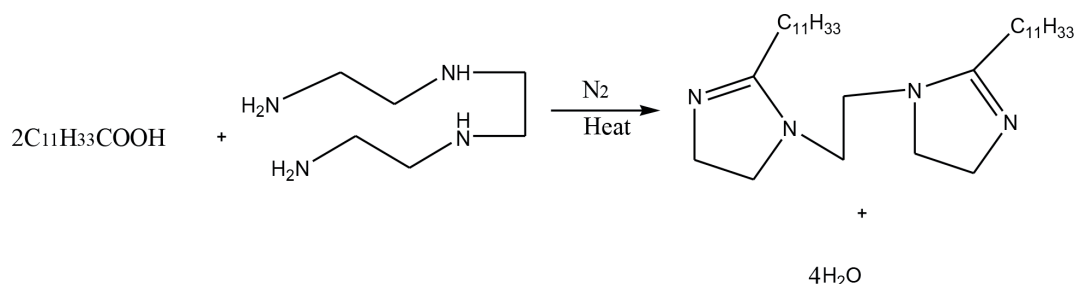


Figure 5.
Synthesis of Bisalkyl-bis-imidazoline intermediate [21].

Isopropyl alcohol or water mixture was added to it with continuation for 8 hours at 80–90 °C. simultaneously, the pH of the solution has been around 8–9 by mixing the 10 wt.% NaOH solution. The supernatant liquid of the obtained product was taken in a beaker and mixed with 95% of alcohol for recrystallization. With the use of anhydrous alcohol, unreacted salts were removed from the solution. Thus, it resulted in the final product by removing the amide using chloroform [21] (**Figure 6**).

3.3 Synthesis of cationic gemini imidazoline surfactants

3.3.1 Synthesis of imidazolines

Tripathy et al. (2016) has synthesized the imidazoline using microwave synthesizer. Different compounds were taken in the beaker such as diethylenetriamine (20 mmol), fatty acids (Myristic acid, stearic acid, Lauric acid, Palmitic acid and Oleic acid- 40 mmol) and calcium oxide (20 g). The reaction was occurred at appropriate temperature as set in microwave. Later on, the mixture was cool down at room temperature. Then it further processed by adding the 80–100 ml of ethyl acetate and boiled, the remaining mixture was filtrated out and dried using vacuum. The optimization has been done and product was yielded at its maximum. The characterization and purity of the product was analyzed by spectrum [33].

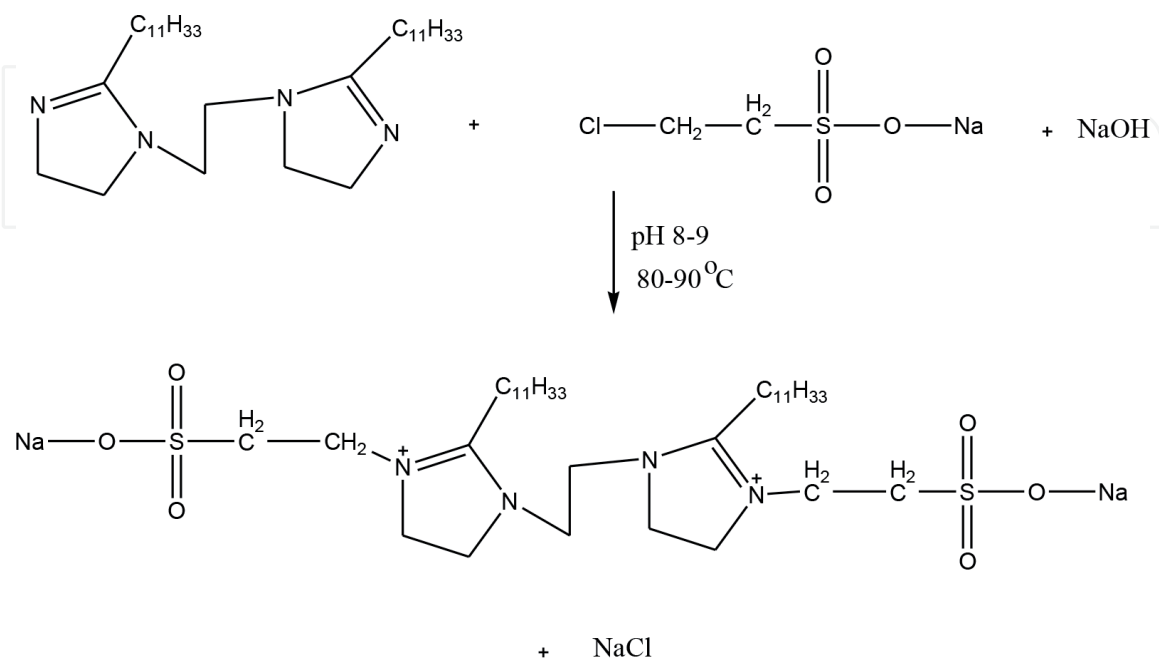


Figure 6.
Quaternization of the Bisalkyl-bis-imidazoline intermediate [21].

3.3.2 Synthesis of cationic Gemini imidazoline using waste frying oil

The synthesis of cost effective gemini imidazoline has also been reported by using waste frying oil like rapeseed oil, soyabean oil etc. The gemini imidazoline thus prepared have been analyzed for their surface active and performance properties. When compared to their monomeric counterparts, these geminis were found to be many folds superior to their corresponding monomeric counterparts [33].

3.3.3 Synthesis of cationic Gemini imidazoline surfactants with carbonate linkage

Tripathy et al. (2016) synthesized gemini imidazoline by the reaction of monomeric imidazoline and di iodoalkyl carbonated under microwave irradiation. Synthesis of di (iodoethyl) carbonate as quaternizing has been achieved by mixing the iodo alkanol and diphenyl carbonate (1:2 molar ratio) acted as carbonate exchange reaction in acetone at room temperature [22]. The resultant product was recrystallized by adding ethyl acetate and acetone (50:50) in it. The obtained product was Gemini imidazoline which further characterized by spectral analysis [33].

3.3.4 Synthesis of imidazoline-based dissymmetric bis-quaternary ammonium Gemini surfactant

Compound (I) N-(3-chloro-2-hydroxypropyl)-N, N-dimethyl alkylammonium chloride was formed by constantly mixing the N, N-dimethyl alkylamine hydrochloride, N, N-dimethyl alkylamine, and epichlorohydrin (1:1:1 molar ratio) for 14 hours in absolute ethanol. A light-yellow mixture has been obtained due to subsequently rotary evaporation of the ethanol. This product was further processed by repeated recrystallization from n-hexane and acetone to attained the white solid crude product. As per the study of this paper, compound (I) produced around 84.30% with the melting point of 47–48°C. The dissymmetric bis-quaternary ammonium salt with imidazoline ring (compound (II)) was synthesized using

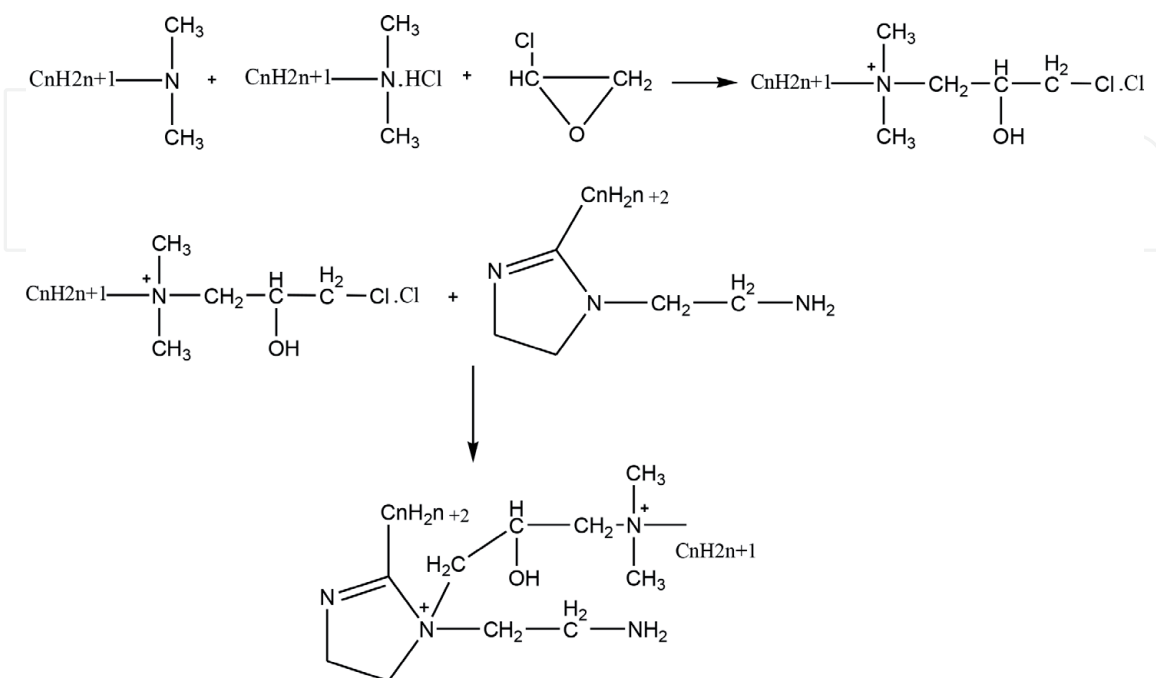


Figure 7.
 Synthesis of imidazoline-based dissymmetric bis-quaternary ammonium Gemini surfactant [34].

alkyl imidazoline and N-dimethyl alkylammonium chloride, N-(3-chloro-2-hydroxypropyl)-N in isopropanol by keeping under the reflux for 10 hours and by putting the excess amount of alkyl imidazoline (10%). The resultant appeared as a waxy compound product. This product was further recrystallized with absolute acetone to obtain the desired compound in the form of a white solid with a melting point of 69–70°C. The characterization of the final product was performed to check the surfactant surfaces using Mass spectra and infrared spectrum, and ^1H NMR (JNM ECP 600 MHz spectrometer) [34] (**Figure 7**).

4. Properties

4.1 Surface tension

Surface tension is the necessary exertion which is obligatory for the enhancement of the surface area of a liquid due to intermolecular force. Surfactant helps in reducing the surface tension of the liquid. An increase in the concentration of surfactants leads to a decrease in surface tension. Gemini imidazoline surfactant-containing stearic acid solution increased in the concentration from 0.1813 to 0.3626 g/l whereas the surface tension decreased from 42.8 to 28.6 mN/m. Again, the process repeated, the concentration of surfactant increased up to 0.6250 g/l leads to a decrease in the surface tension to 27.6 mN/m and a final increase in the concentration to 1.25 g/l and 2.5 g/l but the surface tension remained unchanged [22].

In the same study, the CMC values of 1% aqueous solution of gemini surfactants were found in the range from 0.0016 to 0.0032 mol/l that depends on the alkyl chain length (**Figure 8**). Greater the chain length of hydrophobic alkyl moiety, greater the CMC values of surfactant solutions [22].

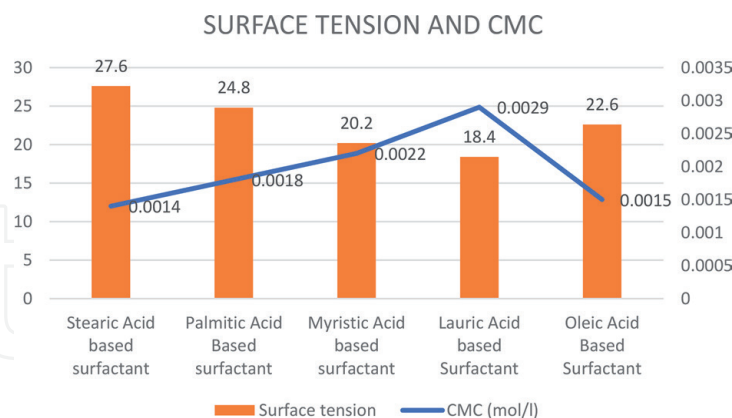


Figure 8.

Variation in surface tension and CMC values with hydrophobic chain [20].

4.2 Dispersion

An arrangement in which scattered particles of one substance dispersed to another substance is known as dispersion phenomena. Surfactants help in stabilizing the dispersion phenomena. Cationic gemini imidazoline surfactant showed stable and good dispersion capability. Gemini imidazoline surfactant-containing stearic acid had a cloudiness of about 4.8 ml that decreased with time. After 5 minutes, it was 3.6 ml and decreased to 3.0 ml after 10 minutes [20, 22]. The trend was found same when the gemini surfactants of different length of hydrophobic chain

have been studied but in addition it was also revealed that decrease in the chain length of hydrophobic group increases the dispersibility of surfactants but the stability of dispersion was found to be decreased (**Figure 9**).

4.3 Softening

Cationic surfactants are used as fabric softening agents. The most common cationic surfactants which are used for softening agents are quaternary ammonium salts, imidazolinium salts, etc. [35]. The softening of surfactants decreases with the decrease in the length of the chain of the alkyl group. When compared with surfactants, it showed that surfactant-containing oleic acid had moderate softening behavior whereas fatty and highest alkyl chain has less softening. Fabrics treated with surfactants found to be soft as compared to untreated fabrics. Therefore, gemini imidazoline surfactants make the fabrics soft.

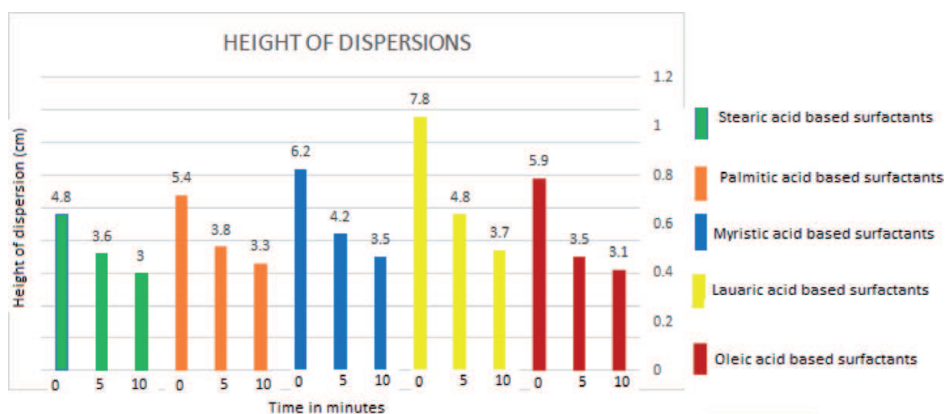


Figure 9.
 Dispersibility of gemini surfactants based on different fatty acids.

4.4 Critical micelle concentration (CMC)

The surface-active agent present in solutions helps in the formation of micelles and this phenomenon is named as Micellization. This phenomenon occurs in critical micellar concentration or slender concentration. The surfactants can lower down the surface tension of the molecule which occurs due to the free monomer concentration and starts the micelle formation. This micelle formation in the solution is termed as critical micelle concentration. CMC is determined by the surface tension of the surfactant. An increase in concentration leads to a decrease in the surface tension until it reaches the critical micelle concentration. It was determined by plotting the graph of surface tension against the algorithm concentration of the surfactant. Critical micelle concentration and surface tension decreased with an increase in the length of the alkyl chain [10]. Zhang et al. research showed the CMC value of Gemini surfactant as 3.2_10_4 mol/L (194.9 mg/L) as per the graph reading in which surface tension plotted against log molar concentration of the surfactant and the breaking point revealed the mentioned value [6].

4.5 Wettability

The capability of a liquid to comes in contact with a surface of a solid and maintains it; this process is known as wettability. The adhesive and cohesive interaction helps in maintaining the interaction between liquid to solid and liquid to liquid. This property of gemini imidazoline surfactant increases with a decrease in the

hydrophobic group length in the chain present in the surfactant. Whereas, the fall in the concentration of gemini imidazoline surfactant resulted in a decreased in the rewet ability and vice-versa [1, 20].

4.6 Inhibitor

Surfactants are used as corrosion inhibitors; they act as a protector on metal surfaces from corrosion. The gemini surfactants are amphiphilic, hence develops an affinity at metal/metal oxide–water interfaces for adsorption phenomena which leads to creating a barrier on metals and metal oxides surfaces and inhibits corrosion [36]. Imidazoline plays a vital role in corrosion inhibition as the imidazoline ring bond with the planar alignment to the surface of the metal. Further studies showed that the imidazoline inhibits the corrosion by blocking, activating, and using energy-related aspects together [37, 38].

4.7 Emulsification

A property of surfactants at the interface. Emulsification is a process that forms an emulsion between two immiscible liquids such as oil suspended in water [36]. Emulsification is an important property for gemini imidazolinium surfactants for the formation of the emulsion. The emulsification power of a surfactant varies with the length of the spacer group. It is directly proportional to the spacer chain length. Stable emulsions are required in drug formulation, cosmetics, solubilizations, etc. [5].

5. Applications

5.1 Biological activity

The antimicrobial activity of surfactants based upon the surface-active properties, hydrophobic chain length, and concentration. Gawali et al. (2019) synthesized the cationic Gemini surfactants and mentioned their application. The synthesized Gemini surfactants were assessed to check the biocidal activity contrary to a variety of bacteria such as *Bacillus subtilis*, *E. coli*, *Staphylococcus aureus*, and *P. aeruginosa*.

The $R = C_7H_{15}$ [2-Octyl-1-diethylenediaminimidazoline based gemini surfactant (GSCTDH)] and $R = C_{11}H_{23}$ [2-dodecyl-1-diethylenediaminimidazoline based gemini surfactant (GSLTDH)] compounds showed good microbial activity. The $R = C_{13}H_{27}$ [2-Tetradecyl-1-diethylenediaminimidazoline based gemini surfactant (GSMTDH)] surfactant was inactive for *Pseudomonas aeruginosa* but showed active behavior for *Bacillus subtilis*, *E. coli*, *Staphylococcus aureus*. The $R = C_{15}H_{31}$ [2-Hexadecyl-1-diethylenediaminimidazoline based gemini surfactant (GSPTDH)] compound showed biocidal activity against *E. coli*, *Staphylococcus aureus*. The GSCTDH surfactant compound containing the highest antimicrobial activity amongst the other Gemini synthesized compounds. As the compound showed the biocidal activity against the bacteria (gram-positive and negative), they can be considered to use as an antimicrobial agent in the form of surfactants. The test result showed the variation in the sensitivity of Gemini compound towards the gram-positive and gram-negative bacteria, they were more sensitive to gram-positive bacteria as compared to gram-negative bacteria. The reason behind that could be the behavior of the outer membrane of the bacteria which was less permeable in the case of gram-negative bacteria [39]. The surfactant having low critical micelle concentration values shows good corrosion inhibitor property due to their absorption quality

at low concentration [40, 41]. Gawali et al. studied this property on carbon steel by making the surfactant with different concentrations at 30 °C in 1 N H₂SO₄ [42].

5.2 Industrial applications

The gemini imidazoline surfactant with quaternary imidazolinium salts is used as a dispersant, emulsifiers, bleach agent, ant-static agent, and fabric softener as they show the better result as compared to the traditional surfactant and also have a mild effect on clothes, to eyes, and their biodegradability. Gemini imidazoline surfactant solubility is low in water [21]. They can be used for drug entrapment, oil recovery, also a probable vehicle for the transference of bioactive particles, for cleaning purpose, used as aerosol application [43].

5.2.1 Corrosion inhibitor

Zhuang et al. examined the corrosion inhibition property of gemini imidazoline surfactant on copper. They synthesized the imidazoline gemini surfactant using saturated fatty acids and studied the property by electrochemical method. Copper was taken in NaCl solution and according to the work, it showed that various factors like pH, surfactant concentrations, and length of carbon chain affects the suppressive efficiency. The inhibition effect was better with the increase in gemini imidazoline surfactant concentration whereas suppressive efficiency is more when the length of the carbon chain is short [13].

Yang et al. synthesized the gemini imidazoline surfactant by adding oleic acid with triethylenetetramine (2:1). They studied the inhibition of carbon dioxide corrosion by linear polarization resistance in sparged beaker testing and concluded that the less concentration of gemini imidazoline was effective as corrosion inhibition when compared with traditional imidazoline and emulsion tendency was less than traditional imidazoline. The synthesized gemini imidazoline with oleic acid has improved film persistency, Higher surface activity, lower critical micelle concentration than traditional imidazoline. Therefore, this is a better surfactant as it is polluting the environment less than conventional imidazoline and also have better corrosion inhibition property [44]. Obot et al. also studied the corrosion inhibitors and concluded that the imidazoline based gemini surfactants are good corrosion inhibitors [37].

5.2.2 Laundry detergents

Gemini Imidazolinium surfactants have antistatic property, maintain the softness of fabrics. The studies showed that the antistatic property of gemini quaternary ammonium salt surfactant helps in reducing the polyester fabric resistance to 107 Ω.S-HSJ-18 and resulted in displaying the finest softening effect which leads to the low down the polyester fabric stiffness to be less than 2 mN·m. The pre-treatment process with KH560, cross-linking monomer N-hydroxymethyl acrylamide (MAM) and N, N-methylene bisacrylamide (MBA) of thermal setting fabric exhibited the greatest outcome for cross-linking that changed the wetting time of the fabric which could be more than 120 min and might stays the same after washing the fabric three-time i.e. 90 mins [45].

5.3 Nanoscience and nanotechnology

Li et al. developed the nanoparticles with a combination of silver and gemini imidazoline surfactants. The silver (Ag) nanoparticles well dispersed in nature

were taken for the synthesis with novel imidazoline Gemini surfactant quaternary ammonium salt of di (2-heptadecyl-1-formyl aminoethyl imidazoline) hexane diamine at room temperature. Characterization of Ag nanoparticles was done by X-ray diffraction, Transmission electron microscopy, Fourier transform infrared, and UV- absorption spectra. The result revealed the enhanced micellized aggregation of gemini imidazoline surfactant in water as well as the Ag particles and the coordination and adsorption phenomena between the Ag nanoparticles and the imidazoline surfactant. It can act as environmentally friendly nanoparticles due to the modification in the surface of synthesized Ag nanoparticles. The developed Ag nano product act as a metal catalyst for methyl orange reduction reaction because of the active adsorption between methyl orange particles and Ag nanoparticles [46].

6. Conclusions

Gemini imidazolines are the surfactants that have been continuously getting explored for their varied application. At the one end where, the pendant structure of imidazoline surfactants make them easily absorbable on to the polar surface on the same time the fatty alkyl chain imparts hydrophobicity thus defending so many polar surfaces by the adverse environmental impact and increase the life of surfaces. Presence of two surfactants molecules with in the molecule, drastically minimize their CMC values thus making the surfactants cost effective. Heterocyclic atom present in the ring of hydrophilic group imparts antimicrobial properties in the molecule thus making the surfactants suitable as antimicrobial agents. Furthermore, their existence in various forms like cationic, amphoteric, nonionic increase their applicability in various more industrial sectors.

Conflict of interest

The authors declare no conflict of interest.

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