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Synthesis and Evaluation of Cationic Surfactants

Amira Mahmoud[a], Wagdy I. El-Dougdoug[a], Mohamed A. Abo-Ryia[a*], Hany I. Mohamed[a*]
[a] *Chemistry Department, Faculty of Science, Benha University, Benha 13518, Egypt*

***Corresponding authors:**

Dr. Mohamed A. Abo-Ryia
Professor, Chemistry Department, Faculty of Science, Benha University, Benha 13518, Egypt
Email: mohamed.aborya@fsc.bu.edu.eg ORCID: 0000-0002-6754-1720

Dr. Hany I. Mohamed
Associate Prof., Chemistry Department, Faculty of Science, Benha University, Benha 13518, Egypt
Email: hany.ibrahim@fsc.bu.edu.eg ORCID: 0000-0002-1733-7801

Abstract

Gemini cationic surfactant was prepared by the quaternization of 2-(dimethylamino)ethyl dodecanoate with 1,3-phenylene bis(2-chloroacetate). Gemini surfactants possess a distinctive chemical structure that sets them apart from traditional surfactants. They contain two hydrophilic heads, and two hydrophobic tails that are connected together by a spacer group as methylene or stilbene. If the properties of the prepared Gemini surfactants are compared with conventional, these surfactants have a higher performance efficiency at lower concentrations so; small amounts are needed. They are more effective at reducing the surface and interfacial tension giving lower values of CMC, also have better aggregation structures which lead to the more economically favored in industrial field. The prepared compound shows good surface properties as suitable emulsifying agent in cosmetics applications.

***Keywords*:** Gemini cationic surfactants, quaternization, surface properties.

1. Introduction

Surfactants are organic amphiphilic molecules made up of two parts: a hydrophilic head, which is polar and soluble in water, and a hydrophobic tail, which is nonpolar and insoluble in water [1-2]. Surfactant term is derived from surface-active agents [2-3], Due to their dual amphiphilic nature, they can aggregate in various shapes called micelles and decrease the interfacial tension between water and oil [4-6]. The efficiency of surfactants can be measured by their tendency to decrease the surface and interfacial tension [5]. Surfactants can be categorized based on the electrical charge present on their hydrophilic head group into four types [3,7]: anionic, cationic, amphoteric, and nonionic [5,8,9]. Surfactants also can be divided according to the source from which it is synthesized into natural surfactant (biosurfactants)that comes from natural sources which characterized by low toxicity [10] cheap, ecofriendly, and more active at high temperature than commercial or synthetic surfactants which are more expensive, and less biodegradable [11]. so; researchers look forward to replacing these synthetic surfactants by a natural one to avoid their limitations and disadvantages while capture the features of natural surfactants [10]. At the beginning of twentieth century, a new type of surfactants called Gemini surfactant or dimeric surfactant appeared, it consists of two hydrophilic heads and two hydrophobic tails per one molecule [12], these two parts are connected by a spacer of methylene or oxyethylene groups [8,13-16]; the spacer can be either hydrophobic or hydrophilic, flexible as methylenes or rigid as stilbene [8]. When both hydrophobic tails are similar, and the hydrophilic heads are identical; Gemini surfactant produces a symmetric structure. If the heads are identical with different hydrocarbon tail, Gemini surfactant is called heterogemini [8]. These compounds have more excellent properties than the conventional surfactants [16], they can give lower interfacial tension values, high heat stability, better aggregation structures [16], and lower values of CMC. we can use a small amount of Gemini surfactants to obtain the same results of conventional surfactants. They can be used in various applications such as medicine, electronics, cosmetics [8], water treatment [17], drug delivery [18], and corrosion inhibitors [19]. Also, can be used as emulsifiers, dispersants [16], and solvents dissolve various types of materials [20,21]. The main objective of this paper is to synthesize natural Gemini surfactants from vegetable oils and provide a substituent to commercial surfactants [10]. Here, we describe the chemical route to synthesize one Gemini cationic surfactant. Characterization of the surfactant produced was done using FT-IR. surface properties of the synthesized surfactants were extensively inspected.

2. Experimental section

2.1. Materials and instruments

All chemicals were used without further purification, lauric acid, N,N dimethyl amino ethanol, and chloroacetyl chloride all obtained from Sigma-Aldrich. para toluene sulphonic acid (PTSA) was obtained from Loba Chemie. Diethyl ether was purchased from Oxford Lab Fine Chem. n.hexane was obtained from PLOBA. Xylene, dichloro methane, anhydrous sodium sulphate, sodium carbonate, ethyl acetate, petroleum ether (40-60 ^{0}C), paraffin oil, methanol, sulphuric acid, Resorcinol, Tri Ethyl Amine, and sodium hydroxide were purchased from Al-Nasr chemical company. FT-IR (ATR or KBr disc) was carried out on Nicolet iS10 FT-IR spectrophotometer.

2.2. Synthesis

Gemini cationic surfactant with a hydrophobic tail of twelve carbon atoms was prepared and the synthetic procedures were explained in the following reactions through three main steps.

***i*. General procedure for the synthesis of 2-(dimethylamino)ethyl dodecanoate (A)**

The compound was prepared as shown previously [6]. Equimolar from N,N dimethyl amino ethanol (0.01 M, 0.889 gram) was esterified with lauric fatty acid (0.01 M, 2.003 gram) in the presence of 0.03 % PTSA as a catalyst and dry xylene as a solvent using dean-stark apparatus, reflux with stirring at nearly 150 ^{0}C till forming one equivalent of water. The produced fatty ester compound was isolated by extraction with petroleum ether, drying the organic layer using anhydrous sodium sulphate (Na_2SO_4)[6] and then the solvent was evaporated till complete dryness.

***ii.* Synthesis of 1,3-phenylene bis(2-chloroacetate) (B)**

Chloroacetyl chloride (0.021 mol, 2.37 gram) was slowly added to a stirred solution of resorcinol (0.011 mol, 1.157 gram) and tri ethyl amine (0.021 mol, 1.66 gram) in 10 mL of dichloromethane at 0 ^{0}C. The reaction mixture underwent stirring at room temperature till the completion of reaction depicted by TLC. to produce dichloro diester compound, The produced diester compound was isolated using methylene chloride for extraction, drying the organic layer using anhydrous sodium sulphate (Na_2SO_4 ,Save the sample till complete evaporation of methylene chloride. [14]

***iii.* Synthesis of the target gemini surfactant (2,2'-(1,4-phenylenebis(oxy))bis(N-(2-(dodecanoyloxy)ethyl)-N,N-dimethyl-2-oxoethan-1-aminium) chloride)**

The obtained dichloro diester (B)(0.01M, 2.63 gram) was refluxed with fatty ester of lauric acid (0.02 M) in the presence of ethyl acetate as a solvent for a long time nearly 90 hours at 70 ^{0}C. After the reaction was finished, the sample was saved till the evolution of ethyl acetate then, washed by diethyl ether several times for additional purification of the final synthesized Gemini cationic surfactant [6] as shown at the scheme -1, the structure of the synthesized Gemini cationic surfactant was investigated using FT-IR.

2,2'-(1,4-phenylenebis(oxy))bis(N-(2-(dodecanoyloxy)ethyl)-N,N-dimethyl-2-oxoethan-1-aminium) chloride

Brown fatty sample, yield=60%, FT-IR(ATR) , at 3351 cm^{-1}(νC-H of aromatic ring),2955.98,2922.64,2852.96 cm^{-1} (νC-H of aliphatic fatty chain),1735.85 cm^{-1}(νC=O of ester),1602.92 cm^{-1} (νC=C), and at 1167.88 cm^{-1} (νC-O).

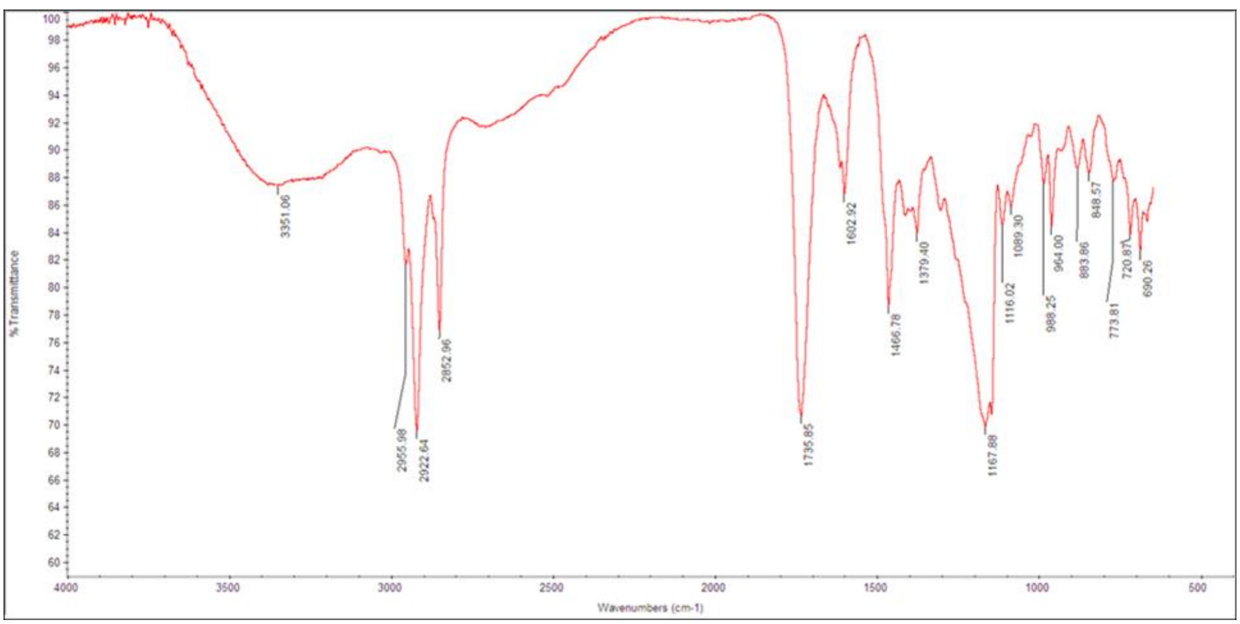


Fig.1. FT-IR result of the Gemini cationic surfactant.

2.3. Surface properties

a) Surface tension measurements

Surface tension is an important property for liquids. Surface tension of distilled water is 72 $mN.m^{-1}$ and surfactants can reduce the surface tension of water. Surface tension values of 0.1 % (wt.) of surfactant solutions were determined using capillarity method. the obtained values were measured at room temperature [16]. the values of surface tension are tabulated at Table-1.

b) Emulsion stability

Powerful shaking of 10 mL surfactant solution (0.1% wt.) with 5 mL of paraffin oil mixed in 25-mL graduated cylinder for two min at 25℃ then, measuring the consumed time to separate the aquas phase (nearly 9 mL) from the emulsion and determined as the emulsion stability. Increasing the time that is required to separate the water indicates the stability of the emulsion formed [22,23,24,25].

c) Foam Height

A solution containing 0.1% by weight of a surfactant was prepared. 100 mL of this solution was placed in a 500 mL graduated cylinder. The cylinder was shaken briefly at a temperature of 25 ℃. The height of the foam that formed immediately after shaking was measured in mm [7,22,23].

d) Stability to hydrolysis

A 10 mL of surfactant solution (0.1 wt.%) was mixed with 10 mL of sulphuric acid 2N or 0.05N of sodium hydroxide placed in a thermostat system at 40 ℃. The solution's stability against hydrolysis was measured by the duration before it turned turbid or opaque [7,25].

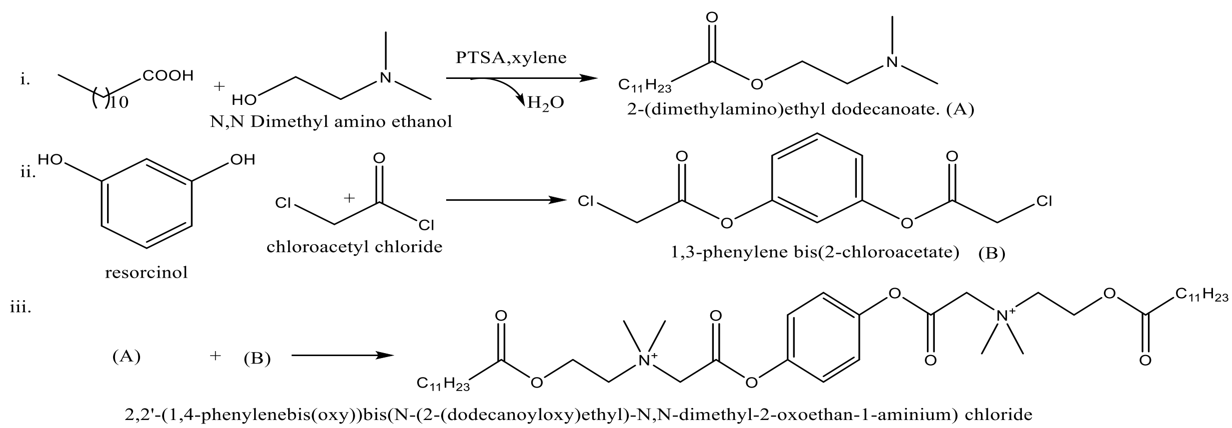
e) Critical micelle concentration (CMC)

A freshly prepared surfactant solution of the synthesized Gemini cationic surfactant using distilled water was prepared many times with various molar concentrations at 25℃ to determine CMC of surfactants using surface tension method [23].

3. Results and Discussion

3.1. Synthesis

Gemini cationic surfactants are very important compounds because of their essential properties and different applications. A new Gemini cationic surfactant was synthesized from lauric fatty acid through the following steps as depicted in **(scheme.1)**. Initially, lauric acid was chemically combined with N,N-dimethyl aminoethanol to form a specific type of fatty ester. Separately, resorcinol was reacted with chloroacetyl chloride to produce 1,3-phenylene bis(2-chloroacetate) [4]. In the final step, the fatty ester was combined with 1,3-phenylene bis(2-chloroacetate) in a process called quaternization, resulting in the desired Gemini cationic surfactant which elucidated using FT-IR(ATR) showed absorption bands at around 3351.85 cm^{-1}, 1735.85 cm^{-1}, 1602.92 cm^{-1}, and 1167.88 cm^{-1} which confirm the presence of aromatic C-H, carbonyl-ester, C=C, and C-O groups [4,10,12,22].



Scheme1. Synthetic route of Gemini cationic surfactant of lauric acid.

3.2. Surface properties

Table-1 shows that the synthesized Gemini cationic surfactant exhibits surface-active properties. This is evident from its ability to reduce the surface tension of water. This reduction occurs as surfactant molecules with hydrophobic tails migrate from the bulk solution to the water's surface.

Table.1- surface properties of the synthesized Gemini cationic surfactant.

Compound No.	Foam h. 0.1% (mm)	Emu. Stab. 10 mmole (min:sec)	Stab. to hyd. acid (min:sec)	Stab. to hyd. base (min:sec)	ST 0.1% (mN/m)	I.F.T 0.1% (mN/m)	CMC*10^{-3} (mol/L)
GCS12	**640**	**8:50**	**36:40**	**2:30**	**31.35**	**14**	**2.9**

a. Emulsion stability

Surfactants have a property of emulsification; it is an essential property leads to their use in different applications as emulsifying agent [10]. The synthesized surfactant has a good emulsifying power so can be used in cosmetic.

b. Foam Height

The synthesized surfactant has a high foaming height so can be used in many industries as washing machines.

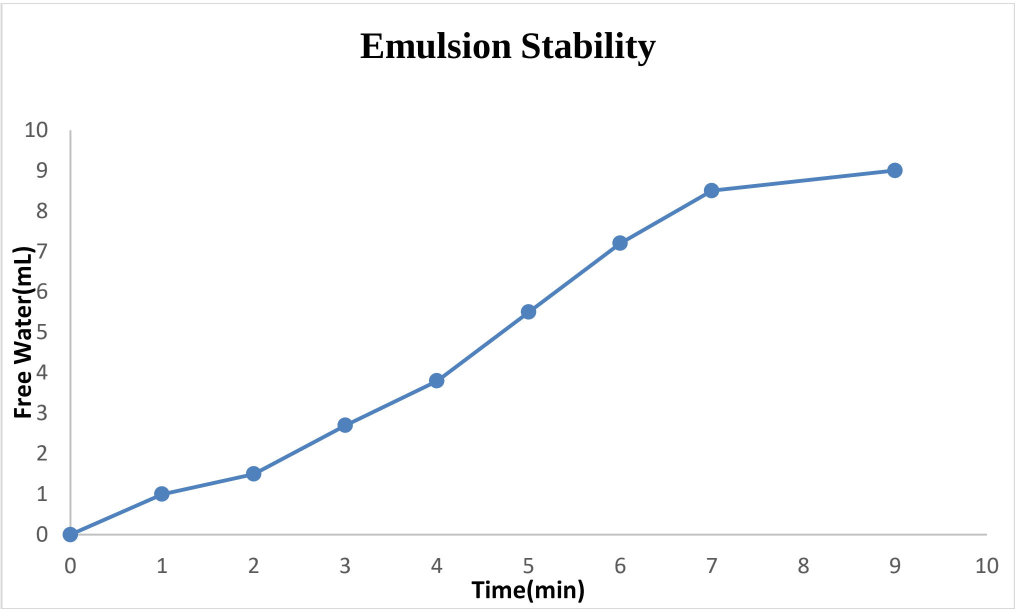


Fig.2. Emulsion stability curve for the synthesized Gemini cationic surfactant.

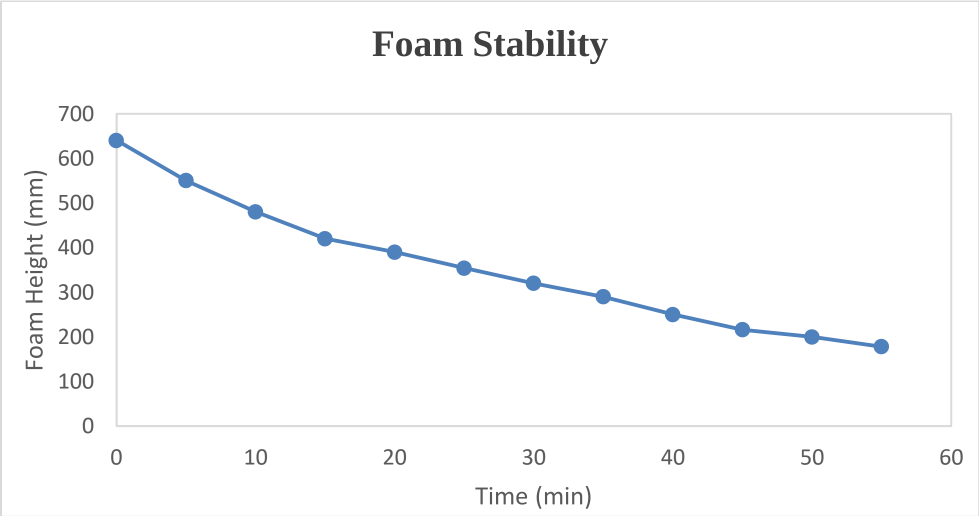


Fig.3. Foam stability curve for gemini cationic surfactant.

c. Stability to hydrolysis

The synthesized Gemini cationic surfactant was exposed to both acidic and basic mediums to study its hydrolysis. It has an ester linkage so hydrolyzed easily in basic medium as shown in table 1, while having a good stability in acidic mediums.

d. Critical micelle concentration (CMC)

The critical micelle concentration is a very crucial parameter for surfactant solution, and it is indicated from the slopes of relation between surface tension and the surfactant concentration in mol.L^{-1} Critical micelle concentration is the point at which the surface becomes saturated of surfactant molecules so, formation of micelles takes place. From the previous data at table 1,we note that the synthesized surfactant has low value of CMC.

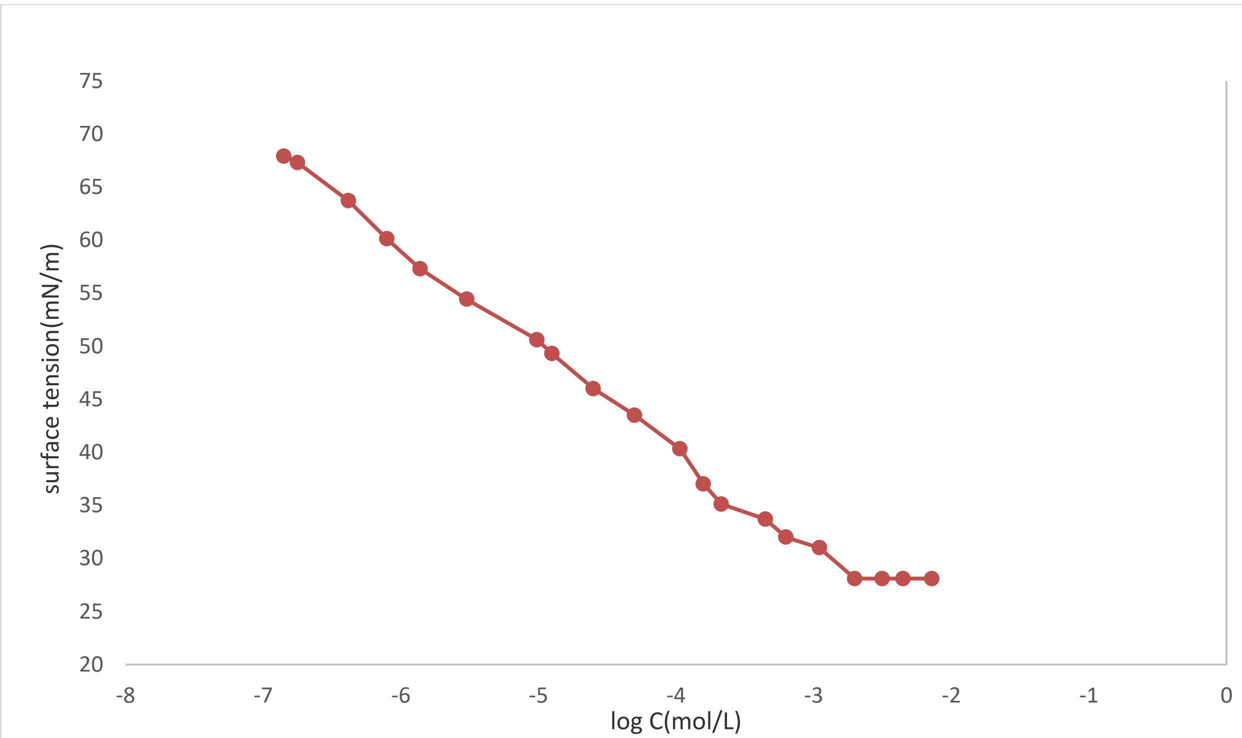


Fig.4. relation of surface tension with log gemini cationic surfactant concentration in aquas solution at 298 K.

4. Conclusion

In summary, new Gemini cationic surfactant was synthesized from natural fatty acid called lauric acid consists of twelve carbon atoms. The chemical structure of the new synthesized Gemini surfactant was investigated and confirmed using FT-IR. Surface properties of the synthesized Gemini cationic surfactant were studied to determine the efficiency of that surfactant. Surface properties like foam stability, emulsion stability, kraft point, stability to hydrolysis in different media, surface and interfacial tension. The studies show that it has a high surface activity, and able to be adsorbed at the interface better than forming micelles in the bulk solution. The synthesized gemini cationic surfactant shows good foaming properties so; can be used in different applications as washing machines, detergents. Also, the synthesized surfactant shows a high emulsifying power, so can be used in various applications as cosmetics. It gives kraft point value lower than zero which means it can be used at lower temperature. Examination that surfactant at basic (0.05N of sodium hydroxide) and acidic media (2N of sulfuric acid) shows that it has a higher resistance to acidic than in basic media, take a longer time to be hydrolyzed in acidic media while needs very short time to be hydrolyzed in basic solutions. This is because the synthesized surfactant has an ester functional group so; it can rapidly hydrolyzed in basic media.

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