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Synthesis and Characterization of Cationic Gemini Surfactants and Study its Applications as Dispersions and Biological Activity

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Abstract: ***Two new cationic Gemini surfactants were prepared to separate Oil – in –Water emulsions, the cationic Gemini surfactants are (A_3 and B_3) that have alkyl chain length of 12 carbon atoms with different spacer . The new compounds were synthesized and characterized by FTIR, and ^1H NMR spectroscopy. The basic surface properties of these novel Gemini surfactants were investigated through measuring the relationship between the electrical conductivity and the surfactant concentration to determine critical micelles concentration (CMC). The new compounds are in many practical applications as treatment O/W emulsion in environmental technology. And Study its efficiency in Biological Activity.***

Keywords: Cationic Gemini surfactants, electrical conductivity, critical micelle concentration, Dispersion, oil in water emulsion

1. Introduction

Geminis are special class of surfactants where two monomeric surfactants (two hydrophilic and two hydrophobic groups) are coupled together by a spacer. Because of the unique structure, gemini surfactants have some superior properties, such as higher surface activity, lower critical micelle concentration (CMC)[1, 2] a higher efficiency in reducing the oil/water interfacial tension, unusual aggregation morphologies, and better wetting, solubilizing, foaming, and antibacterial activities [3 - 5]. The wide application of cationic surfactants in chemical industries, as well as in daily cosmetic and cleaning products, have led to their widespread occurrence in wastewater, groundwater and soils. Moreover, cationic surfactants have been proposed as additive reagents in the mitigation and remediation of organic contaminated soils [6, 7].

In these investigations, we have found that novel quaternary ammonium Gemini surfactants with hydroxyl groups [8-10]. Alkyltrimethyl ammonium bromide is one of the types cationic surfactants that were used to determine the effect on water and oil separation[11].Herein we report the synthesis and the efficiency of dispersing the emulsions of oil in water (O/W) of these Gemini surfactants.

2. Experimental

A. Materials and instruments

The following materials purchased from Sigma – Aldrich company: ethylen glycol (99.5 % purity), Sodium hydrogen sulfate (98% purity), Epichlorohydrin (99.5% purity), petroleum ether dist. Potassium hydroxide (99 % purity), 33% aqueous dimethyl amine, chloroform (99% purity), anhydrous magnesium sulfate (99.5 % purity), methanol (99.8 % purity), 1-bromo dodecane (98 % purity), resorcinol Twice distilled water was used in the preparation of all solutions.

The characterization by ^1H NMR were recorded on a Bruker AM 500 spectrometer. The NMR spectra of the prepared gemini surfactants were recorded in DMSO and chemical shifts recorded were internally referenced to TMS (0 ppm) and Fourier transform infrared (FTIR) verified the structural characters of these new gemini surfactants on a Thermo Electron Corporation Nicolet 380 FTIR spectrophotometer. The CMC values of the surfactant solution were determined from Electrical conductivity with a Jenway PCM3 conductivity meter.

B. Synthesis of (A_3) and (B_3)

There are three steps to get the target compounds:

Synthesis of (A_3):

1) Synthesis of (A) / 3, 3'- (ethane-1, 2-diylbis(oxy))bis(1-chloropropan-2-ol)

To a mixture consisting of ethylene glycol (27.04 g, 0.3 mol), Sodium hydrogen sulfate NaHSO4 (1.00 g, 8 mmol) and water (0.6 ml) in round bottom flask, then added Epichlorohydrin (47.1g, 0.6 mol) drop wise 0 °C. The mixture was stirred for 5 hours and heated to 90 - 100 °C. Until the liquid is transparent yellow which represents the compound (A) [12, 13].

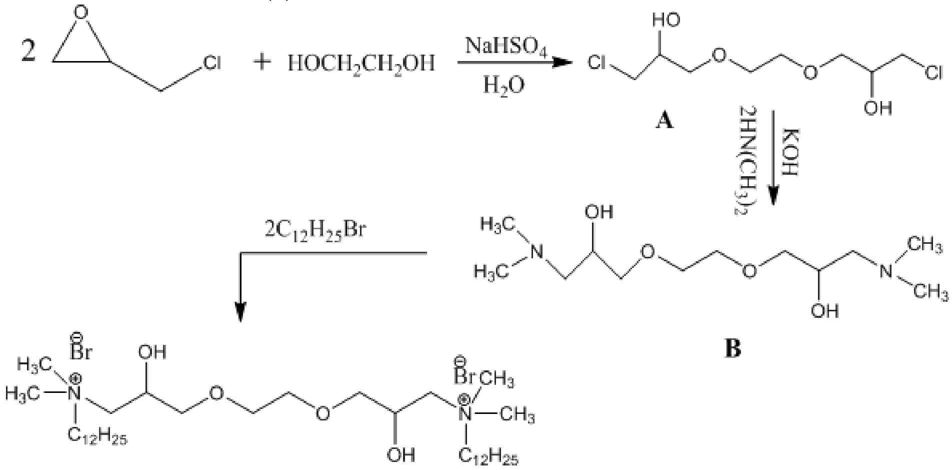
2) Synthesis of (B) / 2, 13-dimethyl-6, 9-dioxa-2, 13-diazatetradecane-4, 11-diol

To a flask containing (0.67 g, 12 mmol) Potassium hydroxide was added 33% aqueous dimethyl amine (0.90 g, 0.02 mol) , then added compound (A) (2.80 g, 0.01 mol) as drop wise with a magnetic stirrer at room temperature to produce precipitate. The mixture was filtered then the filtrate was extracted with chloroform and dried over anhydrous magnesium sulfate The output then evaporates to remove the residual solvent for the purpose of obtaining the compound (B) Which is oil-colored lts is yellow.

3) Synthesis of (A_3) / N, N'-((ethane-1, 2-diylbis(oxy))bis(2-hydroxypropane-3, 1- diyl)) bis(N, N- dimethyldodecan-1-aminium) bromide

To a flask containing 1-bromodecane (1.51 g, 6.84 mmol) and absolute isopropyl alcohol (50 ml) was added compound (A_3) (1.00 g, 3.42 mmol) at room temperature. The mixture was refluxed for 1 hour. To obtain the product (A_3) That is in the form of oily and white. The structure and synthetic route of this surfactant is shown in Scheme (1).

FTIR (NaCl): 3410.15, 2926.01, 2883.58, 1239.83, 1039.63, 728.16 cm−1. 1H NMR (500 MHz, DMSO): δ ppm = 0.854 (t, 6H, 13, 13*), 1.638-1.675{m, 36, (12, 12*)}, 1.729-1.748 (qui, 4H, 10, 10*), 3.245 (s, 12H, 6, 6*, 8, 8*) 3.365 (t, 4H, 9, 9*) , 3.698 (t, 4H, 11, 11*) 3.913- 3.927 (d, 8H, 2, 2*, 4, 4*) , 4.349-4.375 (qui, 2H, 3, 3*) 5.514, (s, 2H, OH)



Scheme 1: Synthetic Route to Gemini surfactant (A_3)

Synthesis of (B_3)
Phenylenebis (oxy)) bis (1-chloropropan-2-ol) 1, 3-(-'1-Synthesis of (A) /3, 3

To a mixture consisting of resorcinol (27.04 g, 0.3 mol), Sodium hydrogen sulfate NaHSO4 (1.00 g, 8 mmol) and water (0.6 ml) in round bottom flask, then added Epichlorohydrin (47.1 g, 0.6 mol) drop wise 0 °C. The mixture was stirred for 5 hours and heated to 90 - 100 °C. Until the liquid is transparent yellow which represents the compound (A) [12, 13].

2-ol propan-)(1, 3- phenylenebis (oxy) bis(1-(dimethylamino'-3, 3 2-Synthesis of (B)/

To a flask containing (0.67 g, 12 mmol) Potassium hydroxide was added 33% aqueous dimethyl amine (0.90 g, 0.02 mol), then added compound (A) (2.80 g, 0.01 mol) as drop wise with a magnetic stirrer at room temperature to produce precipitate. The mixture was filtered then the filtrate was extracted with chloroform and dried over anhydrous magnesium sulfate The output then evaporates to remove the residual solvent for the purpose of obtaining the compound (B) Which is oil-colored lts is yellow.

3- Synthesis of (B_3) / N, N'-((1, 3-phenylenebis(oxy))bis(2-hydroxypropane-3, 1- diyl)) bis(N, N-dimethyldodecan-1-aminium) bromide

To a flask containing 1-bromodecane (1.51 g, 6.84 mmol) and absolute isopropyl alcohol (50 ml) was added compound (B) (1.00 g, 3.42 mmol) at room temperature. The mixture was refluxed for 1 hour.

To obtain the product (B_3) That is in the form of oily and Brown. The structure and synthetic route of this surfactant is shown in Scheme (2).

FTIR (NaCl): 3421.72, 2960.73, 2854.65, 3059.10, 1558.48-1379.10 , 1253.73 , 1111.00 , 721.38 cm−1. ^{1}H NMR (500 MHz, DMSO): δ ppm =0.891 (t, 6H, 16 , 16 *), 1.648 -1.675 {m, 36, (15, 15 *) 1.859-1.871 (qui, 4H, 14, 14*), 3.279 (s, 12H, 11 , 11*, 12 , 12*) 3.384 (t, 4H, 13, 13*), 4.227-4.236 (d, 8H, 6, 6*, 9, 9*), 4.356(qui, 2H, 7, 7*)5.297, (s, 2H, OH) 6.347-6.361(d, t, s, 4H, Ar-H)

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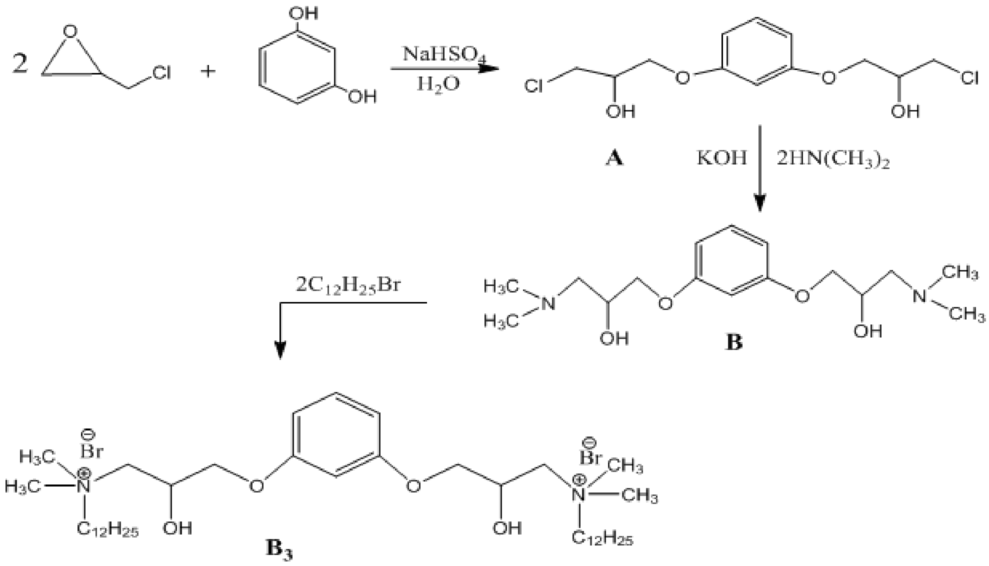

Scheme 2: Synthetic Route to Gemini surfactant (B_3)

3. Results and Discussion

A. Measurement of CMC Values of Surfactant Solutions by Electrical Conductivity

The critical micelle concentration (CMC) of a surfactant is an important physical parameter [14, 15], which can determine it's by the change in the electrical conductance of aqueous ionic surfactant solutions due to cationic ions and anionic ions [16, 17]. The electrical conductivity is usually influenced by solvent and temperature [18, 19] so that have been prepared a series of aqueous solutions of cationic Gemini surfactants then measured their conductivity at 25 °C. The values of CMC were calculated as the intersection of linear parts in the dependence conductivity versus surfactant concentration[20], and can be observed conductivity change linearly (extrusive) with the change of concentration due to the nature and concentration of counter ions in solution and the effect increases with decreasing charge density of the counter ion [21, 22].

Where noted from Figures that impairment of conductivity with reduced concentration of Gemini surfactants, can be attributed to a decline in the number of ions that contribute to the electrical conductivity, which leads to lower it, until a specific point is CMC point then be a simple change in the line as shown in the Figures (1) and (2**).** In addition Bis – quaternary ammonium salts from epichlorohydrin exhibit large intermolecular hydrophobic interaction that make it easy for them to form aggregates in water [23].

Through the results observed when increasing aliphatic tail length reduces the CMC value for surfactants, and the compounds with small polar heads are influenced by the length of the aliphatic tail to a much greater extent than surfactants with large non-ionic polar-regions. Where is observed that the value of CMC to (A_3)
($0.2x\ 10^{-4}$ M) less than (B_3) ($0.5x\ 10^{-4}$ M) [24-26].

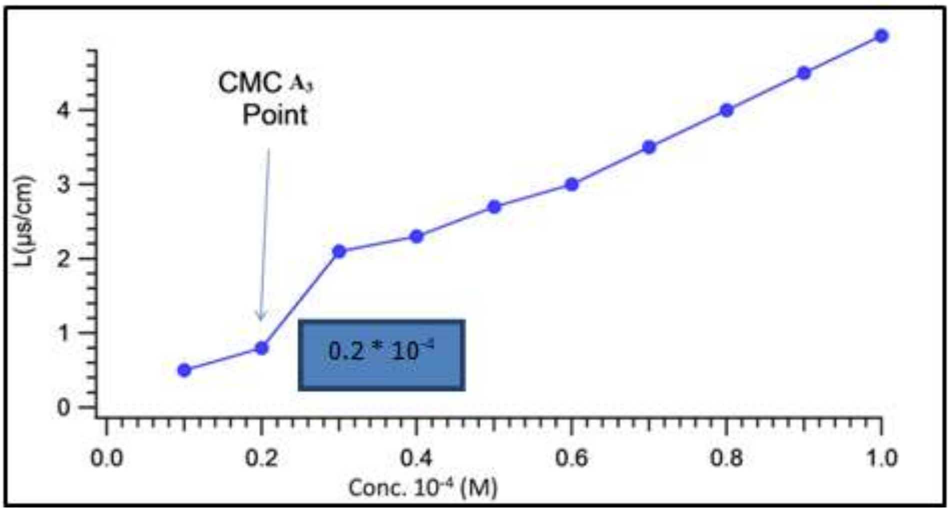

Figure 1: CMC of (A_3) Surfactants

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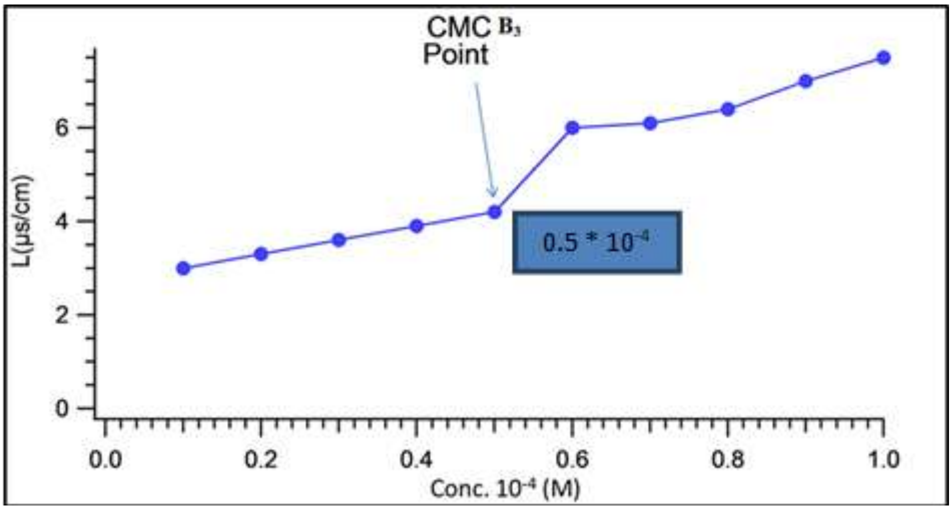


Figure 2: CMC of (B_3) Surfactants

B. Study the Efficiency of Gemini Surfactants as Dispersions

The dispersions were tested by adding 25 ml of water to the test plate and then adding 10 microliters of oil and remaining for a short period until the situation stabilized. Then add 10 µl of the dispersion D(A_3) and D(B_3)[27] Where we notice the spread of oil and be a white spot resulting from the penetration of the dispersion wall between water and oil That the solvent that was selected in the preparation of dispersants is an ethylene glycol, a compound used in the food and pharmaceutical industries and that it is better than water in the industry of dispersants.

The study showed that the compound (A_3) has greater effectiveness of dispersion of oil from the compound (B_3) because of the different bond (spacer) which is more hard in the compound (B_3) so D(A_3) has few values (CMC) and the lower values (CMC) increased activity of dispersions . The polar part becomes far from the non-polar part each part works more freely to increase efficiency so the compound (A_3) is more active.
As shown in Tables (1 and 2) and figures (3 and 4) .

Tables 1: The concentration used and the size of the enlarged aura of the dispersion

The dispersion halo area (cm^2) after a few minutes	Diameter halo dispersion (cm^2) after a few minutes	The dispersion halo area (cm) after a few minutes	Diameter halo dispersion(cm) after a few seconds	The Concentration (ppm)
33.1	6.5	22.0	5.3	50
55.3	8.4	47.7	7.8	100
65.0	9.1	55.3	8.4	200

Tables 2: The concentration used and the size of the enlarged aura of the dispersion

The dispersion halo area (cm^2) after a few minutes	Diameter halo dispersion (cm^2) after a few minutes	The dispersion halo area (cm) after a few minutes	Diameter halo dispersion (cm) after a few seconds	The Concentration (ppm)
3.7	2.2	1.1	1.2	50
7.5	3.1	5.3	2.6	100
13.8	4.2	6.6	2.9	200

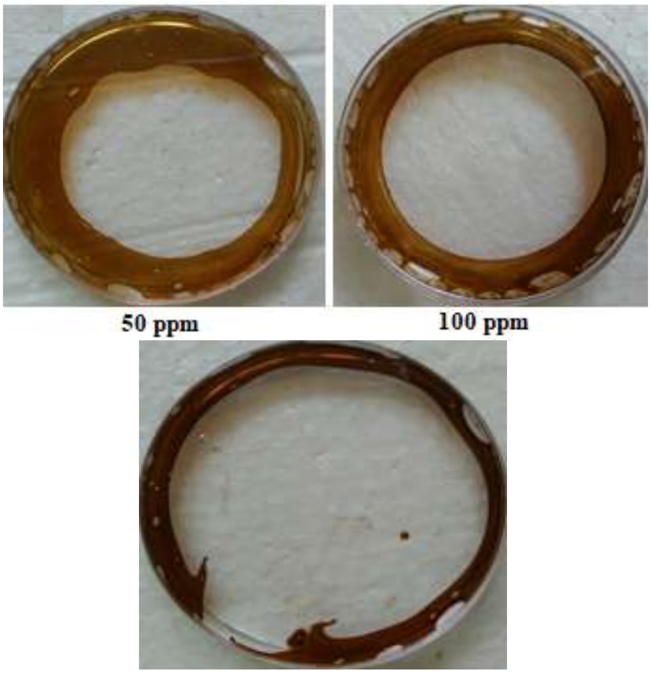
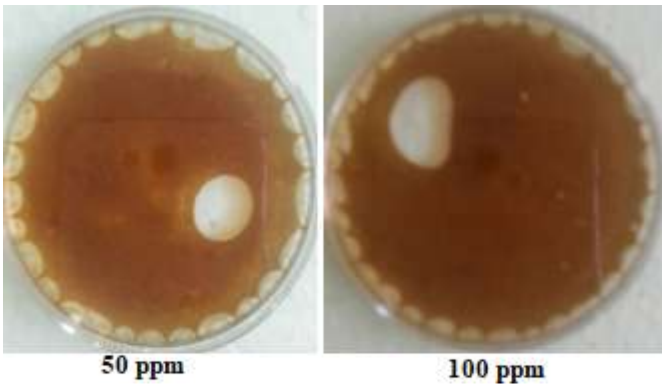


Figure 3: Dispersions of (A_3) Surfactants



200 ppm

Figure 4: dispersions of (B_3) Surfactants

C. Study the Efficiency of Gemini Surfactants as Biological Activity

The biocide activity of gemini surfactants depends on the type of microorganisms. Gram-positive bacteria are more sensitive than the Gram-negative bacteria to ammonium micro biocide. This is due to morphology of the cell membranes. Gram-positive bacteria cell membranes are composed of peptidoglycan layers, which could be easily penetrated by surfactant , whereas Gram-negative cell membranes are mainly composed of lipopoly saccharides and proteins that restrict the entrance of micro biocides [28].

Conventional gemini alkylammonium salts could be modified by the change of number of carbon atoms in the substituent or in the spacer. Compounds, which have 10–14 carbon atoms in the substituent, are more active against bacteria than others [29]. The shorter substituent's are too short to effectively penetrate the membrane. In turn the long substituents have a tendency to coil upwards loosing the ability to penetrate a cell wall. Compared antimicrobial activity of gemini surfactants with flexible and rigid spacers. In the case of surfactants with fourth carbon atom in the spacer, more effective are compounds with unsaturated bond in the linker [30]. Another possibility of stiffening of spacer is to introduce ring. Martín et al. showed that the nature of the ring (aromatic or saturated) does not influence the antimicrobial activity of gemini surfactants [31].

The study showed the effectiveness of the sample (3) represents the compound (A_3) against the Gram-positive bacteria Stap . auveas where was diameter damping about (12 mm) as for the sample (C) represents the compound (B_3) did not show any effectiveness against the Gram-positive bacteria Stap . auveas because of the different group association (spacer). As shown in figures (5and 6).

The samples used to search did not show any effectiveness against Gram-negative bacteria.

Figure 5: Biological Activity against Gram-positive bacteria

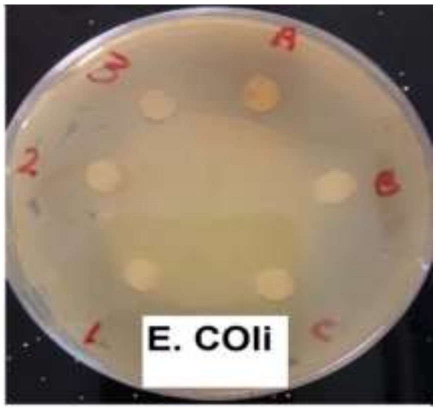


Figure 6: Biological Activity against Gram- negative bacteria

4. Conclusion

The study showed that the compound (A_3) has greater effectiveness for dispersion of oil from the compound (B_3)**.** the compound (A_3) give biological Activity against the Gram-positive bacteria Stap . auveas and the compound (B_3) did not show any biological Activity against the Gram-positive bacteria Stap . auveas .

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