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SYNTHESIS AND CHARACTERIZATION OF NEW GEMINI SURFACTANTS DERIVED FROM IMIDAZOLE AND INDOLE AND STUDY THEIR EFFICIENCY AS DISPERSIBLE AND BIOLOGICALLY EFFECTIVE MATERIALS

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ABSTRACT

In the present study, two sets of stimulants for the gemini surfactants derived from imidazole and indole were prepared, which contain a terminal chain containing eight carbon atoms and a separation between the two heads and two tails of the surface activating substance called 1, 5 – di bromo pentane. The prepared compounds were characterized using the FTIR and ^{1}HNMR. The value of the critical micellization concentration (CMC) was calculated using electrical conductivity, as well as the value of the balance system between hydrophilic and lipophilic groups (HLB) to find out the appropriate application for them. The effectiveness of dispersion of oil spots in (oil/water) emulsions and biological activity on specific types of bacteria have also been studied.

KEYWORDS: CMC, HLB.

1- INTRODUCTION

Gemini cationic surfactants are compounds which are composed of two hydrophilic head groups and two hydrophobic (lipophilic) tails linked by spacer at the head groups or closed to them.[1] The spacer can be either hydrophobic or hydrophilic, It can be rigid or flexible.[2]

In the recent years, much attention has been focused on the development of cationic gemini surfactants, because of their unique ability to form a complex with a variety of negatively charged molecules/ particl and have been widely dispersants, softeners and antistatic

agents.[3] The use of gemini amphiphilic aggregates in gene delivery[4], antimicrobial activity[5] and the synthesis of mesoporus material[6] have developed.

Critical micelle concentration (CMC) of gemini surfactants are usually much lower, up to hundred times, than (CMC) of corresponding monomeric surfactants.[7] The effectiveness of dimeric (gemini) surfactants in lowering the surface tension is also much better than their monomeric analogues.[8] The hydrophilic lipophilic balance is a quasiexperimental measure for choosing the appropriate application of anabolic surface of gemini surfactants.[9] In the present research, we have synthesized a new compounds gemini imidazolium and indolium surfactants by a regio selective ring – opening reaction having one spacer length i.e., $(CH_2)_5$ where n=5. The prepared compounds were used to disperse oil slicks in oil/water emulsions as dispersants and to study their effect as biologically active substances.

2. Experimental Part

2.1- Chemicals

Epichlorohydrine, sodium hydroxide, tetra butyl ammonium bromide, indole, imidazole, 1,5 – di bromo pentane, acetone and ethyl acetate are supplied by the Sigma – Aldrich Company and the octanol is supplied by the Merk company, while the materials (hexane, cyclohexane, aqueous zinc perchlorate, ethelyene glycol, diethyl ether, chloroform and methanol) are supplied by Fischer, Himedia, GT- paker and GCC companies, respectively and crude oil, all the material also were used without purification.

2.2- Synthesis of Gemini Surfactants

2.2.1- Synthesis 2- ((octyloxy) methyl) oxirane

(13g, 0.1mol) octanol was heated in a round bottom to (40 °c) and then added to it (6g, 0.15mol) sodium hydroxide and (0.2g, 0.00063mol) tetra butyl ammonium bromide and continued stirring for half an hour at the same temperature and then added (18.5g, 0.2mol) epichlorohydrine in batches with the maintenance of the temperature between 38-40 °C and the mixture is placed under reflux for (4 hours) until a yellow color product is obtained, then the results is separated using 25 ml of n- hexane and a yield (89%).[10,11]

IR (NaCl, cm^{-1}) (2928, 2858), 1111.

2.2.2- (a): Synthesis 1- (1H- imidazol -1- yl) -3- ((octyloxy) propane -2- ol)

The result of the step 2.2.1 (1.86g, 0.01mol) was added with stirring using a magnetic stirrer and added (0.851g, 0.0125mol) imidazole in the presence of the catalysis (0.1g)

$Zn(ClO_4)_2.6H_2O$ then the mixture under the reflux in (80°C) for (1h) and then continued using TLC and a mixture of solvents cyclohexane and ethyl acetate and at a ratio of (90:10) where the result was yellow color with a yield of (80%).[12]

IR (NaCl, cm^{-1}) 3433, 3155, (2928, 2858), 1554, 1411, 1273, 1111.

2.2.2- (b): The compound **1- (1H- indol-1-yl)-3-(octyloxy) propane-2-ol)** was also prepared using the same steps above and using (1.4643g, 0.0125 mol) indole.[12]

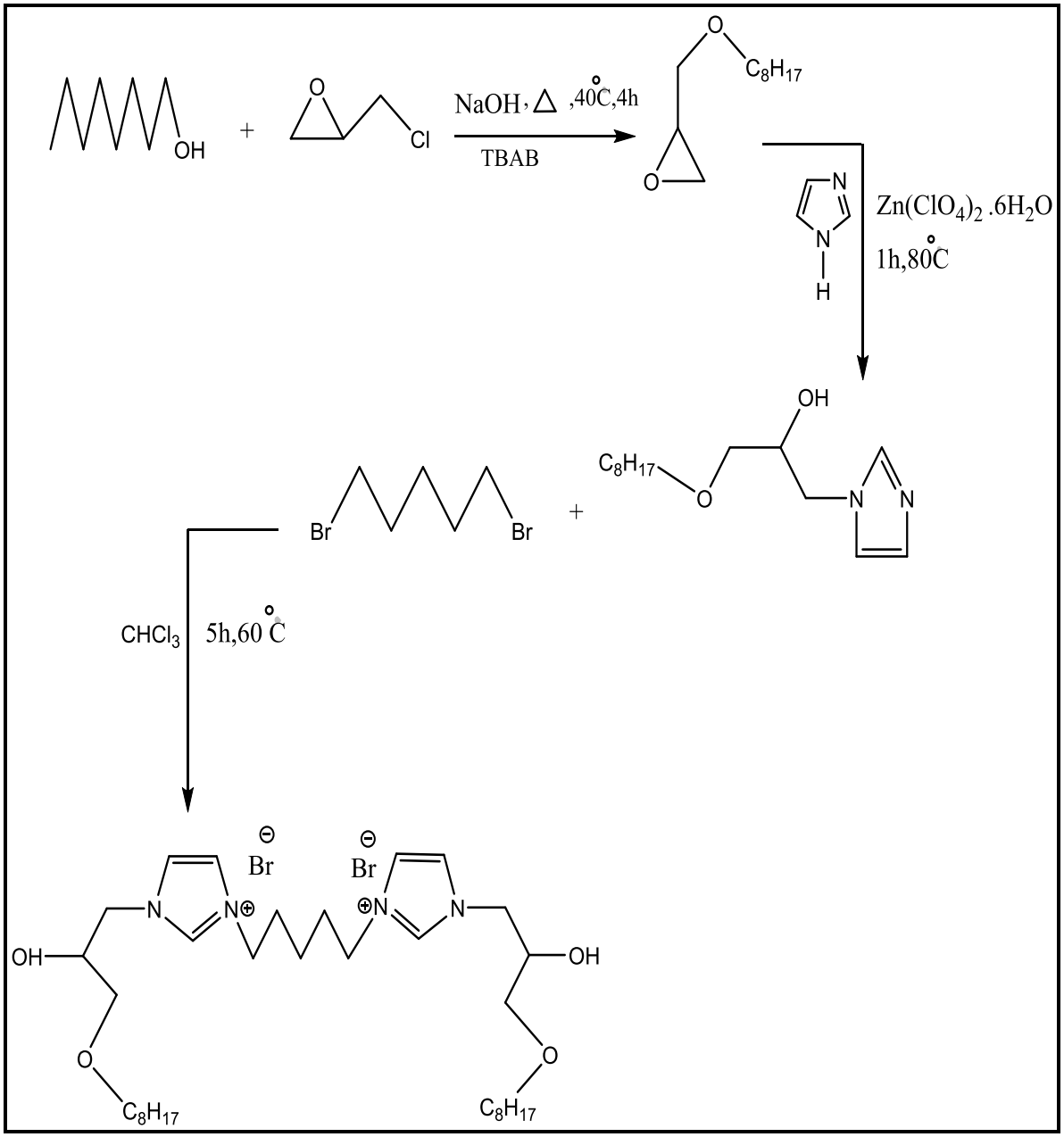
IR (NaCl, cm^{-1}) 3414, 3051, (2928, 2858), 1616, (1458, 1419), 1246, 1099.

2.2.3-(a): Synthesis 3,3'- (pentane-1,5-diyl) bis (1-(2- hydroxy-3-(octyloxy)propyl)-1H-imiddazol- 3-ium) bromide (A)

The result of the step 2.2.2 (a) (2.54g, 0.01mol) has been dissolved in 50ml of dry chloroform and at room temperature with (1.15g, 0.005mol) 1, 5- di bromo pentane where the addition was in small batches with continuous stirring of the mixture. After the addition was complete, the mixture was brought up under the reflux for (5h) at 60°C. After the reaction is completed, the chloroform is separated from the product was washed twice using 50ml of diethyl ether. The result was then deposited with cold aceton and the solvent removed using a rotary evaporator at a temperature of 70 °C for (3h) so that the product (A) was obtained oily yellow with a ratio 72%, as shown as in Scheme (1-1).[13]

IR (NaCl, cm^{-1}) 3365, 3140, (2953, 2926), 1629, 1564, 1259, 1111.

^{1}HNMR: δ 9ppm (S, 2H, OH), δ 7.9-7.4ppm (M, 6H, Imidazole H), δ 4.24ppm (t, 8H, OCH_2), δ 1.85ppm (d, 8H, CH_2N), δ 1.47 -1.45ppm (M, 2H, CH-OH), δ 1.22ppm (M, 30H,CH_2), δ 0.82 -0.81ppm (M, 6H, CH_3).



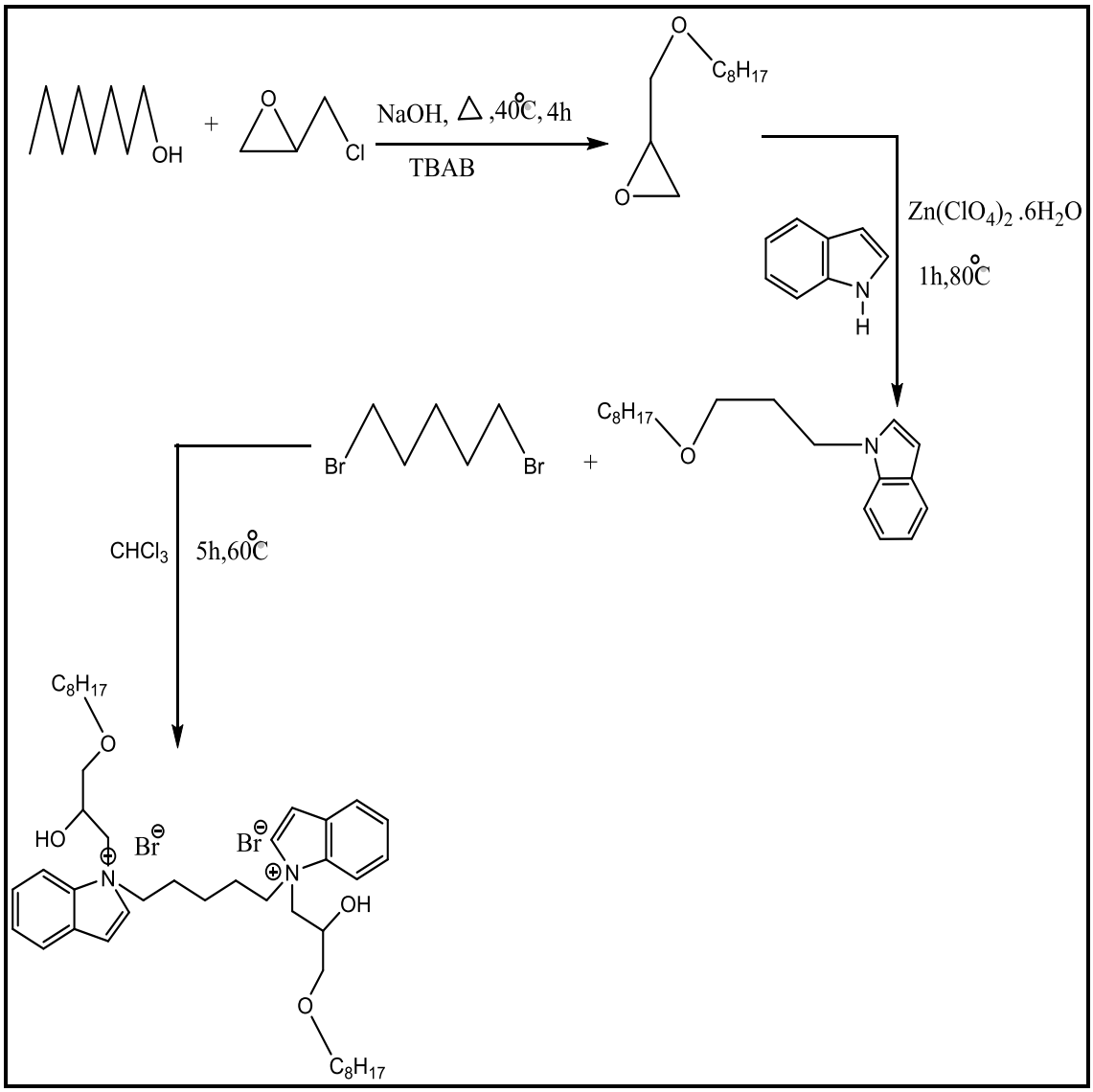
Scheme (1-1): Synthesis compound (A).

2.2.3 (b): The compound 1,1'-(pentane -1,5-diyl) bis (1-(2-hydroxy-3-(octyloxy) Propyl)-1H-indol-1-ium) bromide (B)

Compound B was prepared in the same steps above as using the compound from step (2.2.2 (b)) and dissolving (3.02g, 0.01mol). The product is oily brown with a ratio 59%, as shown as in scheme (1-2).

IR (NaCl, cm^{-1}) 3412, 3072, (2926, 2856), 1611, (1456, 1442), 1246, 1109.

^{1}HNMR: : δ 11.05ppm (S, 2H, OH), δ 7.5 -6.41ppm (M, 12H, Indole H), δ 4.69ppm (t, 8H, OCH_2), δ 1.05ppm (d, 8H, CH_2N), δ 1.48 -1.45ppm (M, 2H, CH-OH), δ 1.24ppm (M, 30H, CH_2), δ 0.86 -0.84ppm (M, 6H, $6CH_3$).



Scheme (1-2): Synthesis compound (B).

3- RESULTS AND DISCUSSION

3.1- Measurement of CMC values of gemini surfactants solutions by electrical conductivity

The critical micelle concentration (CMC) of a surfactant is an important physical parameter[14], which can determine it's by the change in the electrical conductance of aqueous ionic surfactant solution due to cationic and anionic ions.[15] The electrical conductivity is usually influenced by solvent and temperature[16], so that have been prepared a series of

aqueous solutions of cationic gemini surfactants from (0.1* 10^{-4}M - 1* 10^{-4}M) the measured their conductivity at 25 °C.

The CMC were calculated as the inter section of linear parts in the dependence conductivity versus surfactant concentration[17], and can be observed conductivity charge linearly (exrusive) with the charge of concentration due to the nature and concentration of counter ions in the solution and the effect increases with decreasing charge density of counter ion.[18] Therefore, the Gemini imidazolium (A) is more effective (lower CMC value) compared to the Gemini indolium (B) (higher CMC value) for above reason where the CMC value of compound A (0.3*10^{-4} M) and the cmc value of compound B (0.6*10^{-4}M) as shown in Figures 1 and 2.

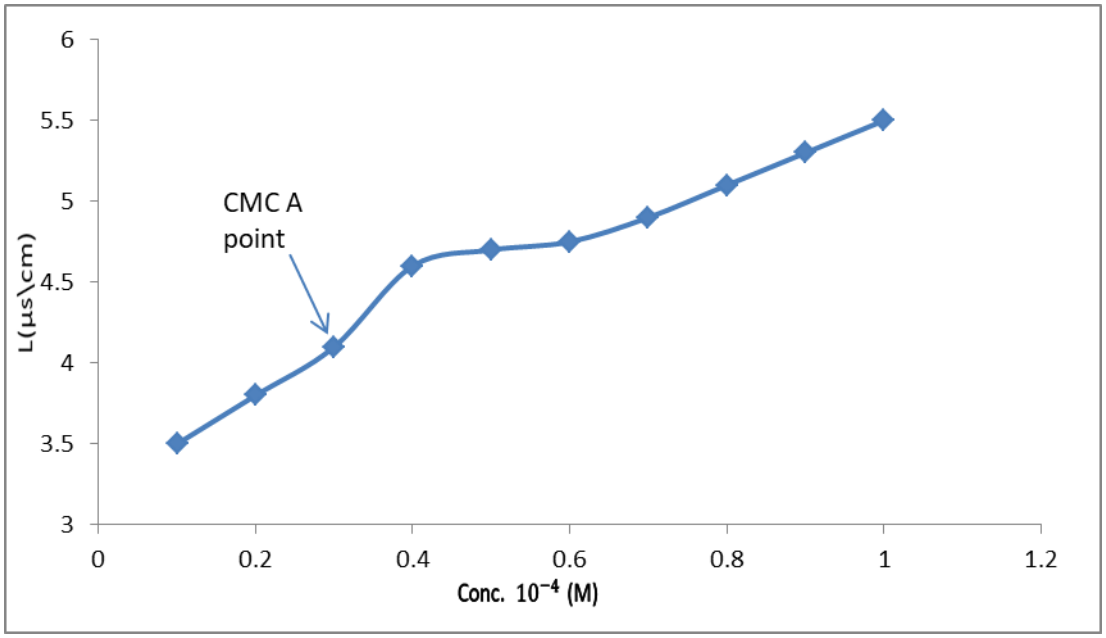


Figure 1: The CMC value of compound A.

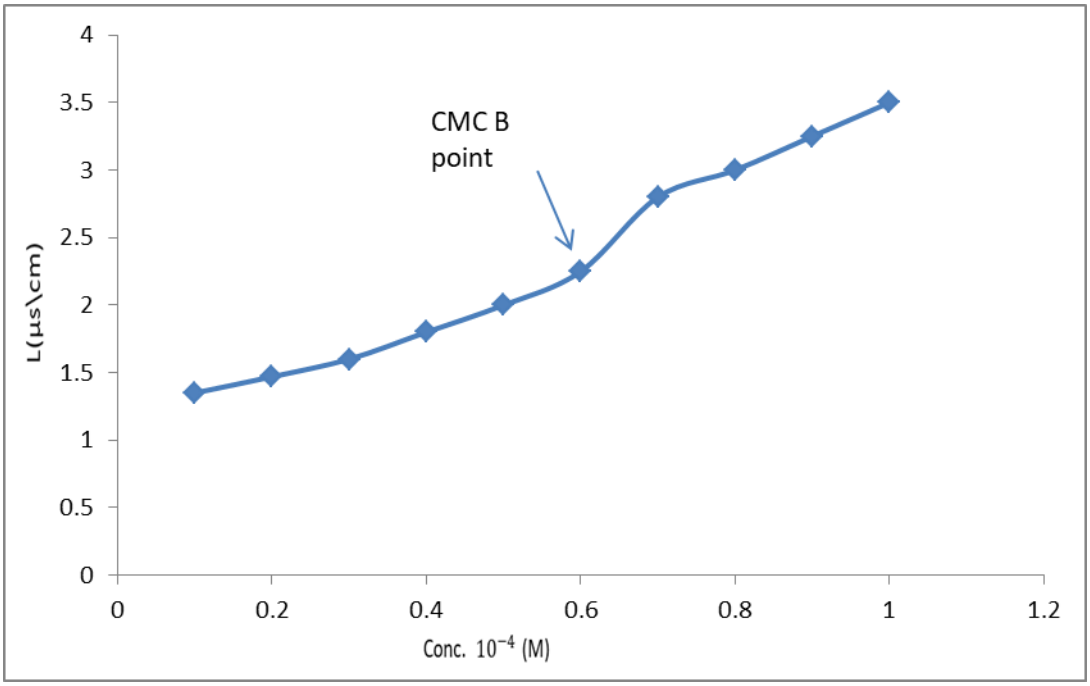


Figure 2: The CMC value of compound B.

3.2- Calculate the value of the balance between hydrophilic and lipophilic groups

The value of HLB was calculated using the Griffin's method as in equation (1) for the compounds A, B to know the applied field for its use and by relying on the literature and comparing it with the calculated values during the current study it was found that they are used in the field of oil emulsion in water (O/W) and as in Table (1).[19]

HLB = 20 * M_h /M ……(1)

Where:

M_h: is the molecular mass of the hydrophilic portion of the molecule.

M: is the molecular mass of the whole molecule.

Table (1): HLB value for prepared compounds.

Compound	HLB value	Field of application
A	**7.7**	**(O /W) emulsion** **(W /O) emulsion**
B	**6.1**	**(O /W) emulsion** **(W /O) emulsion**

3.3 –The use of gemini surfactants as dispersants C(A) and C(B)

Two types of dispersions derived from gemini surfactants containing imidazole and indole were prepared in the composition were prepared at concentrations of 50, 100 and 150ppm by testing them by adding 25ml of water to the test dish and adding (10 µL) of west Qurna oil

and leaving the dish for a short time until the emulsion settles after it (10 µL) of the dispersant was added to the prepared dishes and with the above concentrations where an increase in the dispersion action was observed by increasing the concentration and as in Tables 2 and 3, where it was found that dispersal C(A) is more effective dispersal than C(A) due to the difference of the vertical clear group of water which is more effective due to its high polarity by comparison with dispersal C(B). So it is CMC value of (A) dispersant less than (B) because the less the value of CMC increased the effectiveness of the dispersion.[20,21]

Table (2): Concentration used and dispersive aura size C(A).

Concentration (ppm)	Diameter of the Corona Dispersion (cm) after a few seconds	Halo space Dispersion (cm^2) after a few seconds	Diameter of the Corona Dispersion (cm^2) Five minutes later	Halo space Dispersion (cm^2) Five minutes later
50	5.8	26.4	6.5	33.1
100	7.4	42.9	8.2	52.7
150	8.1	51.5	8.9	62.1

Table (3): Concentration used and dispersive aura size C(B).

Concentration (ppm)	Diameter of the Corona Dispersion (cm) after a few seconds	Halo space Dispersion (cm^2) after a few seconds	Diameter of the Corona Dispersion (cm^2) Five minutes later	Halo space Dispersion (cm^2) Five minutes later
50	2.2	3.7	2.6	5.3
100	3.2	8.0	3.8	11.3
150	4.5	15.8	5.6	24.6

3.4- Study of the biological activity of the prepared gemini surfactants

The biological activity of chemical surfactants is depended on the type of microorganism. cram positive bacteria ***stap. auveas*** are more sensitive than negative cram bacteria ***E. coil*** for ammonium compounds and this reson is due to the morphology of cell membranes. The cell membranes of the ***stap. auveas*** are made of glycan peptides, which can be easily penetrated by surfactants, while the cell membranes of the ***E. coil*** consist of fatty sugars and proteins that restrict the entry of surfactants easily.[22]

Therefore, the results of the biological activity of Gemini surfactants (A and B), Against the positive bacteria ***stap. auveas***) showed the values of the diameter of the inhibition zone 30 and 20mm while the value of the Gemini Surfactants (A and B) ***E. coil*** 28 and 15mm as shown in Table (4).[23] The reason for this is attributed to high effectiveness that the gemini surfactant (A) due to presence for the vertical group that is highly amenable to imidazole

which has the ability to penetrate the membrane of positive and negative bacteria of gram, in contrast to the gemini surfactant (B) that gave good efficacy against the ***stap. auveas*** because of the ease of penetrating the cell membrane, while any negative did not show efficacy a gainst because of the cellular membrane composition, which is difficult to contain as well as easily penetrate the vertical range is less polar and larger size of the polar group in the article A.[24]

Table (4): The inhibition diameter to the gemini surfactants against positive and negative gram bacteria.

Bacteria	A	B
Stap. aureus	**30**	**20**
E. coli	**28**	**15**

4- CONCLUSION

During the present research, the results related to the gemini surfactant (A) and the dispersed prepared from them C(A) are more effective dispersing of the (oil/water) emulsion and more effective biological than substance (B) and the dispersed prepared C(B) because of possession of article (A) strong polar group with high ability to penetrate the separation membrane between oil and water and is able to penetrate membranes positive and negative bacteria for the gram.

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