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Amidoamine double tailed cationic surfactant based on dimethylaminopropylamine: Synthesis, characterization and evaluation as biocide

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ABSTRACT

Three amidoamine cationic surfactants with double tailed were prepared and their chemical structures was confirmed using spectroscopic analysis like FTIR and ^{1}H NMR. The surface parameters of the amidoamine surfactants were determined from surface tension and conductance measurements. The double tailed amidoamine surfactant shown low critical micelle concentration than conventional surfactants with their dependence on chain length and temperatures. Thermodynamic parameters clarified the tendency of surfactants to adsorb at interface than to form micelle and both of the two processes depend on the alkyl chain and temperature. The prepared surfactants were evaluated against microorganism showing that they have good biological activity against both Gram positive and negative bacteria but they have no effect on fungi.

1. Introduction

Surfactants are amphiphile compounds (bifunctional molecules) that contain polar or ionic head group (cationic, anionic, nonionic or zwitterionic) attached to a large hydrophobic part. Typically, the hydrophobic part is an alkyl group with at least eight –CH_2– units. The surfactants are characterized by its ability to self-associate to form association colloids called micelles, the concentration at which it formed called critical micelle concentration. Micelles have interfacial regions containing ionic or polar head groups [1]. They have widespread importance and industrial applications such as detergents, paints, coatings, inks, adhesives, demulsification [2], textile processing, drilling mud, petrochemical recovery, corrosion inhibitors and biocides in petroleum industry [3–4]. Quaternary ammonium compounds have scores of uses because of their affinity for negatively charged surfaces and adsorption of these molecules depends mainly on certain physicochemical properties such as the presence of heteroatoms including oxygen, sulfur, nitrogen and phosphorus atoms and multiple bonds in the molecule through which they are adsorbed on the metal surface [5–8]. Due to the ability of surfactant to adsorb on the interfaces and to form micelle, it is used in nanotechnology in controlling the size and shapes of the nanoparticle [9]. The similarity in chemical structure of quaternary ammonium compounds and cellular constituents eases their destructive action toward microorganisms especially anaerobic bacteria called sulfate reducing bacteria (S.R.B) in souring systems. These bacteria are mainly sulfate reducers and their growth frequently causes severe corrosion problems in oil well pipes which lead to the economic losses as well as environmental health and safety hazards caused by the activity of stabilized mixed culture containing sulfate reducing bacteria (SMC-SRB) [10,11]. The presence of an amidoamine functional group in a surfactant helps in enhancing its biodegradability and in reducing its aquatic toxicity. Intermediates produced in the degradation process of amidoamine were found to be biodegradable and less toxic [12]. Therefore, this work aimed to prepare the amidoamine cationic surfactants with double tailed from dimethylaminopropylamine (DMAPA). As known derivatives based on DMAPA can be used in fuels as cloud point reducers, dispersants, and stabilizers for prevention of deposits or icing, reduction of octane number requirements and corrosion inhibitors for lubricants [13–14]. Due to the self-immunity of microorganism toward the conventional biocides, the use of cationic surfactant was greatly demanded [15–18]. In the present work, we introduced amide group in the cationic surfactant in order to increase the biodegradability and decrease their aquatic toxicity. The surface and thermodynamic properties like, critical micelle concentration (CMC), effectiveness (π_{cmc}), efficiency (Pc_{20}), maximum surface excess (Γ_{max}), minimum surface area (A_{min}), free energy of micellization (ΔG^{o}_{mic}) and free energy of adsorption (ΔG^{o}_{ads}) were determined beside the biocidal activity against fungi and bacteria.

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2. Experimental

2.1. Materials

All the chemicals used in the synthesis process of amidoamine surfactants were of analytical grades and used without more purification; dimethylaminopropylamine (DMAPA) 98%, decyl bromide 99%, dodecyl bromide 98%, hexadecyl bromide 98% and tetradecanoic acid 99% were purchased from Sigma-Aldrich Chemicals Co. The solvents (ethyl alcohol absolute and diethylether) are high grade and purchased from El-gomhoria Chemical Co.

2.2. Instruments

The chemical structure of the new prepared amidoamine cationic surfactants was characterized by; FTIR Spectra using ATI Mattsonm Infinity Series™,Bench top 961 controlled by Win First™ V2.01 Software (Egyptian Petroleum Institute) and ^{1}H NMR by Spect Varian, GEMINI 200(^{1}H 200 MHz) in DMSO-d_6 (National Research Institute). The surface tension for all prepared surfactants was measured using Tensiometer-K6 Processor (KrÜss Company, Germany) using the ring method.

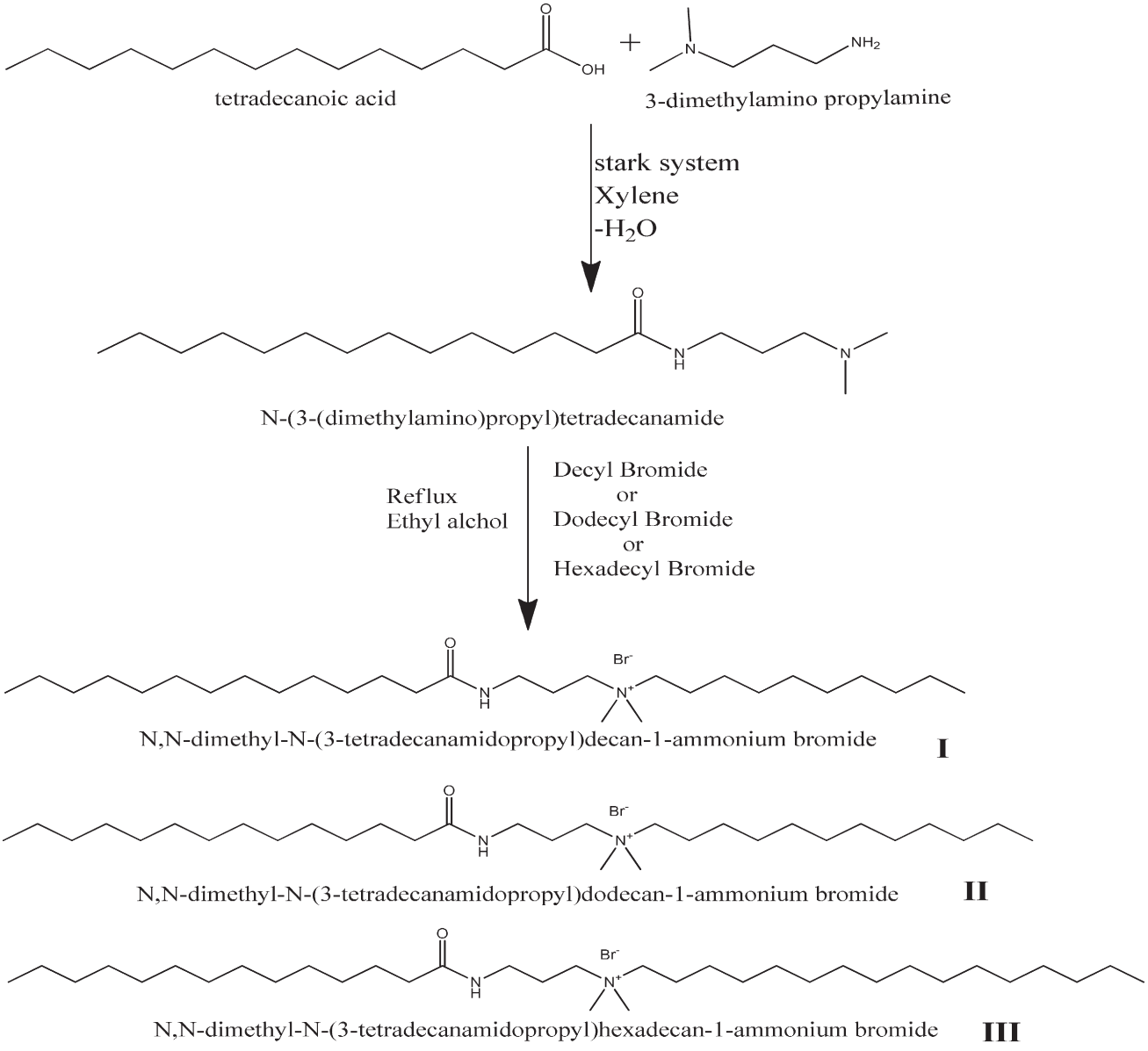
2.3. Synthesis of amidoamine cationic surfactants

2.3.1. Synthesis of N-(3-(dimethylamino) propyl)tetradecanamide derivatives

1,3-dimethylamino-1-propyl amine (DMAPA) (0.1 mol.) was dissolved in 120 mL xylene then 0.1 mol. of tetradecanoic acid was added with 0.01% p-toluene sulphonic acid as a catalyst. The reaction mixture subject to reflux at 138 °C until complete removal of reaction water (0.1 mol., 1.8 mL) using Dean–Stark apparatus. The solvent was evaporated under vacuum rotary evaporator. Petroleum ether was used to get rid of the used catalyst [19].

2.3.2. Synthesis of N,N-dimethyl-N-(3-tetradecanamidopropyl)alkan-1-aminium bromide derivatives

The prepared N-(3-(dimethylamino) propyl)tetradecanamide (0.1 mol.) from the previous step was refluxed with fatty alkyl bromide (decyl bromide, dodecyl bromide and hexadecyl bromide) (0.1 mol.) in



Scheme 1. General procedures for synthesis of double tailed cationic surfactants.

120 ml ethanol as solvent from 30 to 40 h depending on the alkyl chain length. Then it cooled at room temperature. The solvent was evaporated under vacuum and the residue subject to recrystallization using diethyl ether. The obtained amido-amine cationic surfactants named I, II and III and the general procedures for the synthesis were depicted in Scheme 1.

2.4. Measurements

2.4.1. Surface tension (γ)

Surface tension of freshly aqueous solutions of synthesized amido-amine cationic surfactants with concentration range from 1×10^{-2} to 1×10^{-8} M was measured at three different temperatures 25, 40 and 60 °C on tensiometer-K6 Processor using the ring method. The surface tension of pure water was initially obtained for each experiment for instrument calibration. Between the measurement runs, the ring was initially cleaned with pure water, then acetone. The apparent surface tension values were measured a minimum of 3 times for each sample within 2 min interval between each reading and the recorded values were taken as the average [20]. The CMC values were determined from the abrupt change in the slope of surface tension (γ) versus [log c]) plots.

2.4.2. Antimicrobial activities against bacteria and fungi

The antimicrobial activities of the new synthesized surfactants were measured against a wide range of organisms comprising bacteria and fungi. The tested bacteria were Gram-positive (*Bacillus pumilus* and *Micrococcus luteus*) and Gram-negative (*Pseudomonas aeruginosa* and *Sarcina lutea*), the used fungi were *Candida albicans* and *Penicillium chrysogenum*. The different species of tested organisms were obtained from the Operation Development Center, Egyptian Petroleum Institute, Egypt. The used technique for determination of the antibiotic activity was filter-paper disc agar diffusion [21]; the procedures were as follow:

1. Inoculate flask of melted agar medium with the organism to be tested.
2. Pour this inoculated medium into apetri dish.
3. After the agar has solidified, a multi-lobed disc that impregnated with different antibiotics laid on top of agar.
4. The antibiotic in each lobe of disc diffuses into medium and if the organism is sensitive to a particular antibiotic, no growth occurs in a large zone surrounding that lobe (clear zone).
5. The diameters of inhibition zones were measured after 24–48 h at 35–37 °C (for bacteria) and 3–4 days at 25–27 °C (for yeast and fungi).
6. Measure each clear zone and compare between them to determine the antibiotic, which is more effective.

2.4.3. Biocidal activity against sulfate reducing bacteria (SRB)

The inhibition activity of the prepared compounds on the sulfate reducing bacteria growth was measured using the serial dilution method. SRB-contaminated water was supplied from Agiba Petroleum Co.(West Desert, Egypt). The used water was subject to microbial inhibition test. The test has been conducted according to ASTM D4412-84 [22]. The tested water was subjected to growth of about 10,000,000 bacteria cell/ml. The prepared amidoamine double tailed cationic surfactants were tested as biocide for the SRB by dose of (1×10^{-3}, 1×10^{-4}, 5×10^{-5} and 1×10^{-5} M). The system was incubated to contact time of 3.0 h; each system was cultured in SRB specific media for 21 days at 37–40 °C.

3. Results and discussion

3.1. Structure confirmation

3.1.1. FTIR spectra

The chemical structures of the new series from amido-amine cationic surfactants were confirmed using FTIR spectroscopy. The three amido-amine cationic surfactants show nearly the same bands in infrared spectra, so we will explain the spectra of compound 2 for examples. Fig. 1 shows the FTIR of compound (II) which confirm the conversion of acid to amide through disappearance of the hydroxyl group of carboxylic acid which ranged from 2400 to 3400 cm^{-1} (broad band) and appearance band for amide NH at 3363 cm^{-1} and shifting the band of carbonyl from acid region to amide region at 1651 cm^{-1}. The prepared cationic surfactants show stretching vibration band of –C–H aliphatic symmetric and asymmetric at 2854 and 2920 cm^{-1} respectively in

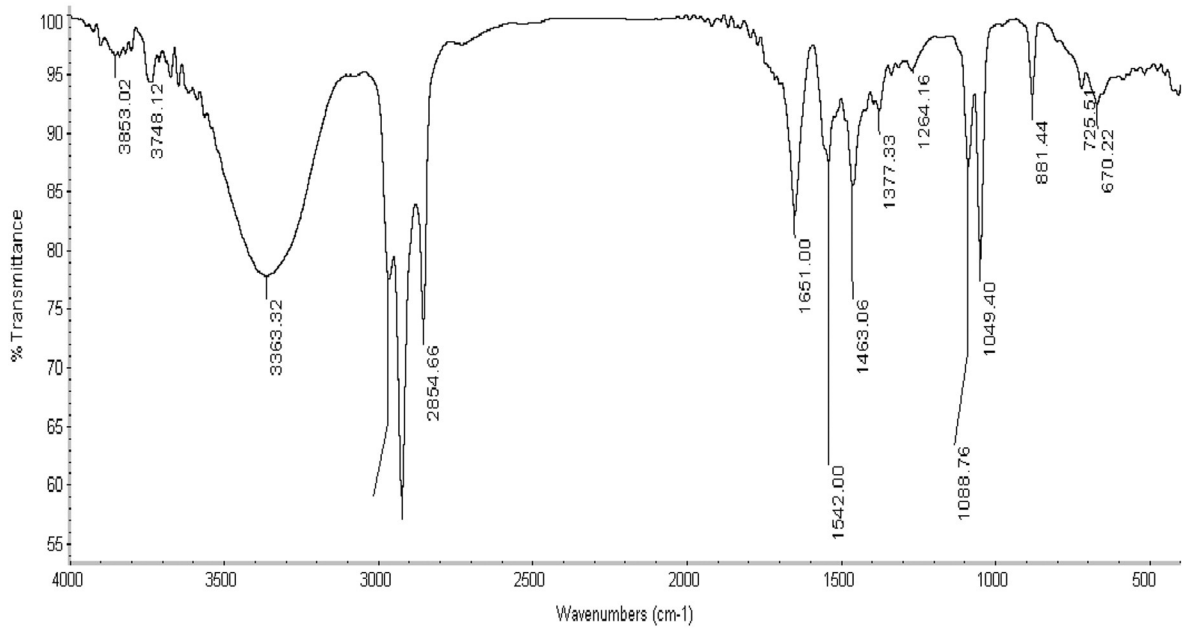


Fig. 1. IR spectrum N,N-dimethyl-N-(3-tetradecanamidopropyl)dodecan-1-aminium bromide (II).

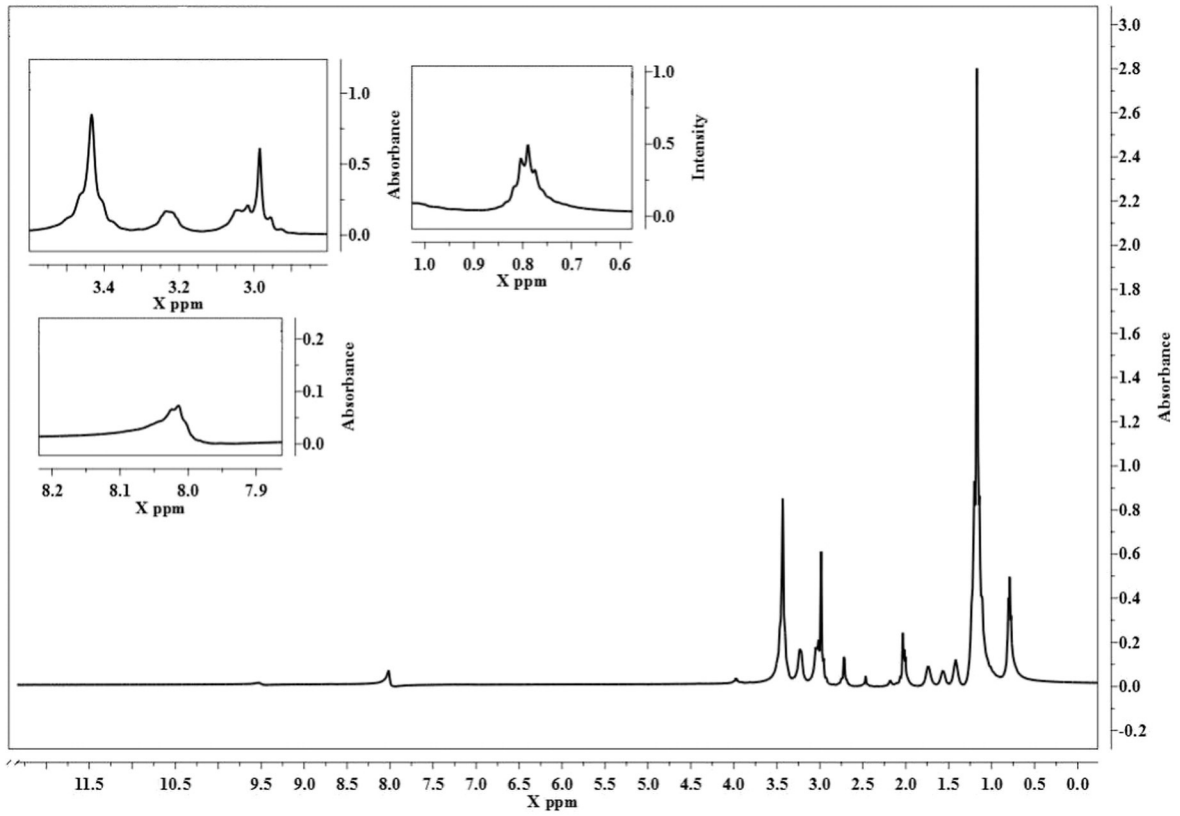


Fig. 2. ^{1}H NMR spectrum of N,N-dimethyl-N-(3-tetradecanamidopropyl)decan-1-aminium bromide (I).

addition to –CH_2 bending at 1377 cm^{-1}, −CH_3 bending at 1463 cm^{-1} and absorption band at 1049 cm^{-1} corresponding to C–N bond.

3.1.2. ^{1}H NMR spectra

The number and distribution of proton in the prepared amido-amine cationic surfactant were confirmed by ^{1}H NMR spectra. Fig. 2 show the ^{1}H NMR spectra of N,N-dimethyl-N-(3-tetradecanamidopropyl)decan-1-ammonium bromide (I) showing signals at: δ = 0.804 (t,6H,**$2CH_3$** alkyl chain); δ = 1.17–1.202 (m,34H, $\_COCH_2CH_2$**$(CH_2)_{10}$**CH_3, $N^{\oplus}CH_2CH_2$ **$(CH_2)_7CH_3$**); δ = 1.419 (m,2H, $COCH_2$**CH_2**$(CH_2)_{10}CH_3$); δ = 1.739 (m,2H, $N^{\oplus}CH_2$**CH_2**$(CH_2)_7CH_3$); δ = 2.034 (m,2H, $N^{\oplus}$-CH_2**CH_2**CH_2NH); δ = 2.721 (t,2 H, CO**CH_2**$CH_2(CH_2)_{10}CH_3$); δ = 3.017 (t,4H, –**CH_2**$N^{\ominus}(CH_3)_2$**CH_2**–); δ = 3.237(t,2 H, CONH**CH_2**); δ = 3.433 (s,6H, $–CH_2N^{\ominus}$**$(CH_3)_2$**CH_2–) and δ = 8.024 (m,5H,CH_2CO**NH**CH_2).

3.2. Conductometric study of double tailed cationic surfactants

The conductivity of the prepared three cationic surfactants was measured at three different temperatures 25, 40 and 60 °C at different aqueous concentrations to cover the pre- and post-micellar region was studied. Figs. 3 & 4 show the relation between the specific conductivity and aqueous concentration of prepared surfactant, where this technique has been employed to investigate the effect of hydrophobic chain and temperatures on the critical micelle concentration, which obtained graphically from the intersection between the two lines. The

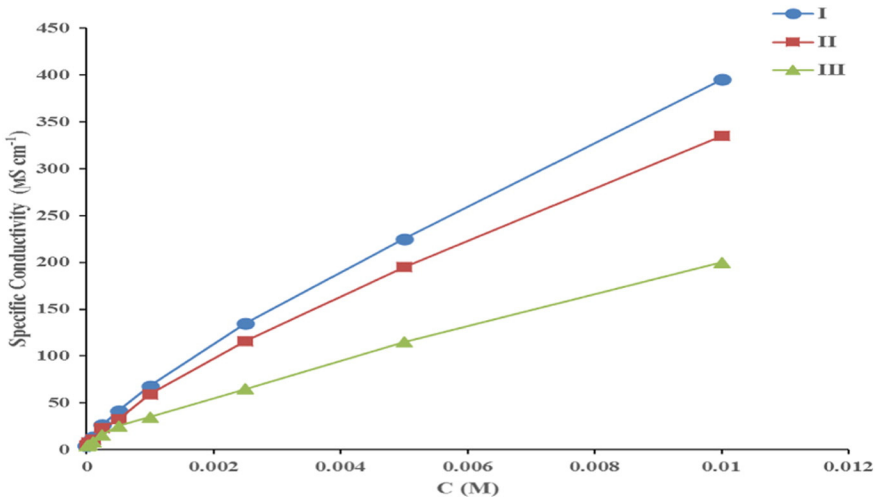


Fig. 3. The plots of specific conductivity against concentrations of the prepared cationic surfactants (I, II and III) in distilled water at 25 °C.

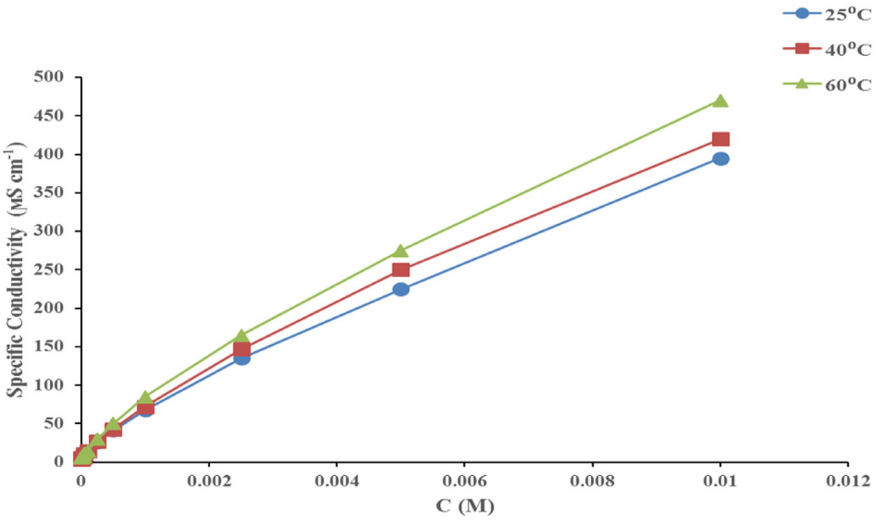


Fig. 4. The plots of specific conductivity against concentrations of the prepared cationic surfactants (I) in distilled water at 25, 40 and 60 °C.

degree of counter ion dissociation (α), has been obtained according to Frahm's method which correspond to the ratio between the slope of the postmicellar region to premicellar one (Frahm's method is approximate and it neglects the contribution of the micelle to conductivity above the CMC therefore, leads to larger <alpha> values) [23]. The determined critical micelle concentration and degree of counter ion dissociation were listed in Table 1. From Figs. 3 & 4, we noted a remarked increase in the conductivity with concentration of prepared surfactants, due to increasing dissociated ion in solution. Decreasing in the conductivity with increasing in the chain of prepared double-tailed amidoamine cationic surfactant as shown in Fig. 3 and as appeared in Table 1 through values of counter ion dissociation return to decreasing the number of cation–anion interaction by increasing the molecular weight [24–25]. Also by increasing the hydrophobic chain length of the prepared surfactant in aqueous system, the hydrophobicity increases and hence the hydration decreases consequently the charge density of the micelle increases so the counter ion will bind more so the conductivity decreased [26–27]. Fig. 4 shows increase in the specific conductivity by elevating the temperature from 25 to 60 °C for the prepared cationic surfactant (I) as an example. This trend confirmed by degree of counter ion dissociation values in Table 1; where it decreases by rising the temperature, α values were 0.404, 0.425 and 0.438 for prepared amidoamine cationic surfactants (II), at 25, 40 and 60 °C respectively. The increase in α values with temperature is a result of two opposing effects and the magnitude of them determines the trend of conductivity with temperature. Rising the temperature will induce the dissociation of counter ion from the head group of surfactant, an effect that in turn increases the conductivity, if this effect is predominant than the columbic force between counter ion and head group of surfactant, the conductivity increases [28–30].

3.3. Critical micelle concentration (CMC)

The critical micelle concentration of the prepared amidoamine double-tailed cationic surfactants has been obtained graphically from surface tension and conductance measurements. Figs. 3–4 show the relation between both the specific conductivity obtained from conductance measurements and aqueous concentration of desired surfactants and the intersection between the two lines represents the critical micelle concentration. While Figs. 5–7 represent a plot between surface tension and aqueous concentration of double tailed surfactants and the abrupt change in the curve points to critical micelle concentration. The critical micelle concentration (CMC) obtained from the two techniques is listed in Table 1, and it was found that CMC obtained through conductance measurements is higher than that obtained from surface tension, which can ascribed to premicellar formation [31]. By analyzing the data of CMC in Table 1, it was found that it decreases by lengthening the hydrophobic chain length and increasing temperature as shown in Fig. 8. Increasing the tail length of the prepared amidoamine cationic surfactant, the hydrophobicity increases thus the free energy of the aqueous system will increase so the surfactant monomers aggregate into clusters in which the tail will be interior to decrease the interaction with the polar medium thus free energy decreases, consequently the CMC decreased [32]. In micelle formation, the hydration around the hydrophilic increase compared to monomers that observed by abrupt increase in conductivity as in Fig. 4, due to increasing the hydration decreases the binding between the counter ion and head group. When micelle starts to be formed, we notice steady in the values of surface tension as shown in Figs. 5–7, due to the micelle formed in the bulk not in the surface. Rising the temperature was accompanied by a decrease in CMC as shown in Fig. 8 and Table 1. As we know, the temperature has

Table 1
The surface properties of synthesized cationic surfactant at different temperatures.

Comp.	Temp. °C	CMC[a]/(mM·L^{-1})	CMC[b]/(mM·L^{-1})	α	$C_{20} * 10^{-6}$ (mol·L^{-1})	π_{CMC}/ (mN m^{-1})	$\Gamma_{max} * 10^{-10}$ (mol·cm^{-2})	A_{min}/ A^2	CMC/C_{20}
I	25	0.423 ± 0.02	0.463 ± 0.01	0.415 ± 0.01	6.12	37.98 ± 1	0.87	189.89 ± 1	69.18
	40	0.251 ± 0.01	0.351 ± 0.02	0.433 ± 0.01	3.58	35.75 ± 0.8	0.69	240.91 ± 2	70.14
	60	0.113 ± 0.015	0.177 ± 0.015	0.451 ± 0.02	1.58	33.81 ± 0.7	0.61	270.18 ± 2	71.34
II	25	0.215 ± 0.015	0.279 ± 0.02	0.404 ± 0.01	3.02	40.19 ± 0.5	0.85	195.04 ± 1	71.34
	40	0.067 ± 0.015	0.084 ± 0.02	0.425 ± 0.01	0.91	37.94 ± 0.6	0.67	247.48 ± 2	73.56
	60	0.042 ± 0.02	0.046 ± 0.015	0.438 ± 0.01	0.56	35.21 ± 1	0.59	280.12 ± 2	75.86
III	25	0.086 ± 0.02	0.087 ± 0.01	0.382 ± 0.01	1.32	37.19 ± 0.5	0.83	199.27 ± 2	64.93
	40	0.019 ± 0.015	0.033 ± 0.01	0.404 ± 0.02	0.29	34.91 ± 0.8	0.58	286.95 ± 2	68.52
	60	0.011 ± 0.01	0.022 ± 0.02	0.412 ± 0.02	0.15	32.53 ± 1	0.52	321.43 ± 4	69.79

[a] The values obtained from surface tension measurements.
[b] The values obtained from conductometric measurements.

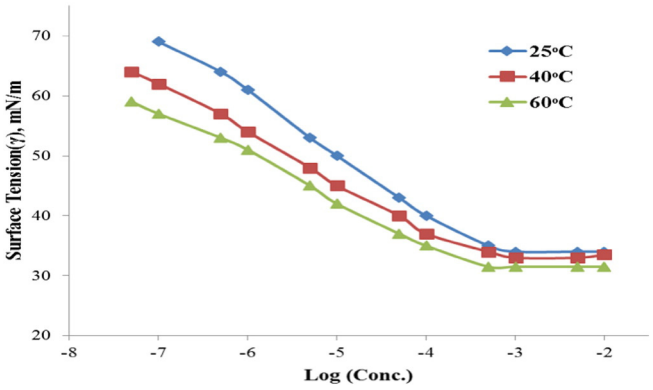


Fig. 5. The surface tension against log concentration of compound (I) at different temperatures.

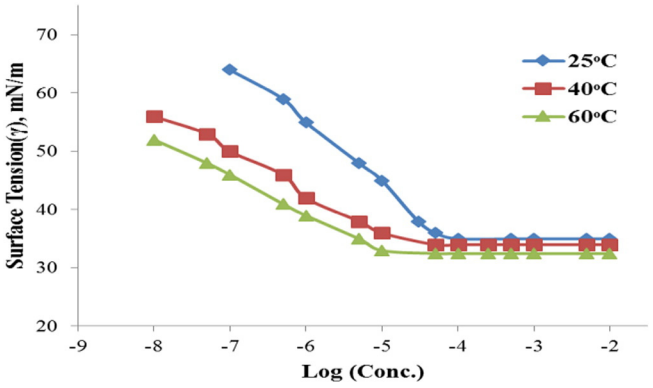


Fig. 7. The surface tension against log concentration of compound (III) at different temperatures.

two opposing effects, the former is decreasing the hydration around hydrophilic head by which the surfactant favor micelle formation; while the second effect is the disruption of the water structure around the hydrophobic tail by which the surfactants disfavor micellization, therefore the net effect is the sum of the two opposing effects. From the obtained data in Table 1, the predominant effect is the former so CMC decreased [32–35].

3.4. Effectiveness and efficiency of double-tailed cationic surfactants

The values of surface tension of prepared double-tailed cationic surfactants at critical micellization have been obtained from surface tension measurements and these values have been used in the determination of the effectiveness of surfactants (π_{CMC}) from the following equation:

$$\pi_{CMC} = \gamma_o - \gamma_{CMC}$$

The effectiveness represents the difference in the values of surface tension at the critical micelle concentration (γ_{CMC}) and at blank water without surfactants (γ_o). Table 1, shows values of π_{CMC} of amidoamine cationic surfactants and the more effective surfactant gives the more reduction in surface tension at critical micelle concentration, which can be explained according to CMC/C_{20} values in Table 1; the greater CMC/C_{20} is, the greater the ability of surfactant to reduce surface tension at CMC. Table 1 showed that CMC/C_{20}, increase from compound I to surfactant II then it decrease at surfactant III, from that the prepared surfactant II has higher tendency to decrease surface tension at CMC, meaning it is the more effective one. The values of π_{CMC}, were 37.98, 40.19 and 37.19 mN/m at 25 °C for surfactant I, II and III respectively, from that the prepared amidoamine cationic surfactant with twelve-carbon chain length (II), is the more effective one in reducing surface tension at CMC, as appeared from values of CMC/C_{20} in Table 1 which has the greater value [36–37]. The higher value of π_{CMC} for surfactants II reflects the condensed nature of the monomolecular film at water/air interface, while the lower value of π for surfactant III indicated that the film at water/air interface is an expanded film.

The concentration of surfactants is required to make a reduction in surface tension by 20 mN/m, known by efficiency (C_{20}) of surfactants under certain temperature and specific system. These values obtained from surface tension measurements and listed in Table 1, from which we note that by increasing both the hydrophobic character of prepared amidoamine double-tailed cationic surfactants and temperature, the efficiency increases, in another meaning the concentration is required for reducing the surface tension by 20 decrease. This can be explained on the basis that by increasing the hydrophobic chain length, the hydrophobicity increases leading to increasing the free energy of aqueous system, so the surfactants with higher chain move more rapidly to the surface in a way to decrease the free energy resulting from the interaction between polar water structure and hydrophobic character, so accumulation at surface can occur at lower concentration [38–39].

3.5. Maximum surface excess (Γ_{max}) and minimum surface area (A_{min})

The maximum surface excess is the concentration of surfactant molecules at the interface per unit area, which depends mainly on the hydrophobic chain length and the temperature. The values of maximum

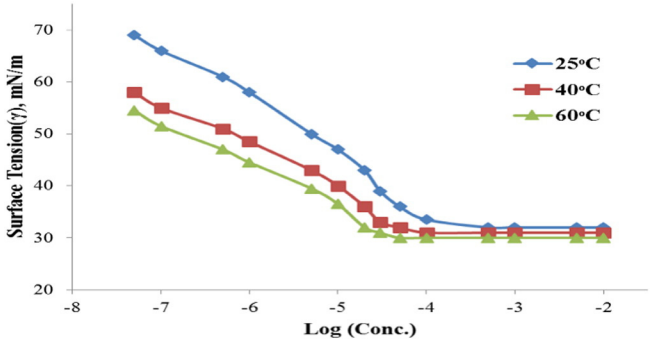


Fig. 6. The surface tension against log concentration of compound (II) at different temperatures.

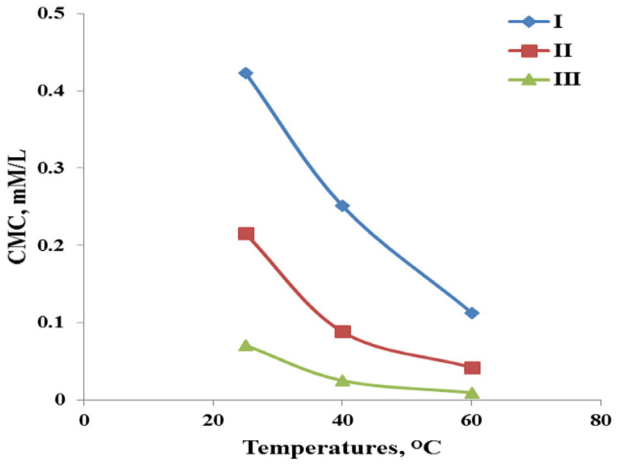


Fig. 8. Effect of temperatures & hydrophobic chain length on critical micelle concentration values of prepared cationic surfactants.

Table 2
Micellization and adsorption thermodynamic parameters of the prepared cationic surfactants.

Comp	Temp. °C	ΔG^{o}_{mic} kJ mol^{-1}	ΔH_{mic} kJ·mol^{-1}	ΔS_{mic} kJ·mol^{-1}.K^{-1}	ΔG^{o}_{ads} kJ·mol^{-1}	ΔH_{ads} kJ·mol^{-1}	ΔS_{ads} kJ·mol^{-1}·K^{-1}
I	25	−46.28 ± 0.3	–	–	−50.82 ± 0.3	–	–
	40	−50.17 ± 0.5	30.91 ± 0.2	0.259 ± 0.02	−55.69 ± 0.5	45.92 ± 0.2	0.324 ± 0.02
	60	−56.15 ± 0.7	43.48 ± 0.1	0.299 ± 0.011	−61.89 ± 0.7	41.36 ± 0.1	0.310 ± 0.012
II	25	−49.28 ± 0.6	–	–	−54.06 ± 0.6	–	–
	40	−55.85 ± 0.5	81.31 ± 2.5	0.438 ± 0.014	−61.63 ± 0.5	96.38 ± 2.4	0.504 ± 0.15
	60	−60.88 ± 0.2	22.94 ± 0.7	0.252 ± 0.01	−67.05 ± 0.2	23.34 ± 0.6	0.271 ± 0.01
III	25	−53.68 ± 0.4	–	–	−57.54 ± 0.4	–	–
	40	−61.65 ± 0.3	104.62 ± 5.6	0.531 ± 0.02	−67.11 ± 0.3	132.69 ± 5.4	0.638 ± 0.02
	60	−67.96 ± 0.1	37.31 ± 1.1	0.316 ± 0.015	−74.05 ± 0.1	41.62 ± 1.1	0.347 ± 0.016

surface excess Γ_{max} calculated from surface tension measurements using the slope below the critical micelle concentration ($\delta\gamma/\delta \log c$) in Gibb's adsorption equation [40].

$$\Gamma_{max} = -(1/2.303\ nRT)(\delta\gamma/\delta \log c)_T$$

Where R is the gas constant, n is number of active species (n equal 2 for monovalent cationic surfactant, equal 3 for Gemini surfactant with monovalent counter ion and 2 for Gemini surfactant with divalent counter ion) and T is the absolute temperature.

Minimum average surface area is the average area (in square angstrom) occupied by each monomer adsorbed at the system interface. A_{min} values give information about the angle between surfactant monomer and the interface [41].

The minimum surface area (A_{min}) of prepared double tailed cationic surfactants has been calculated using Gibb's adsorption equation:

$$A_{min} = 10^{16}/\Gamma_{max}N$$

The determined Γ_{max} and A_{min} values were listed in Table 1, increasing both temperature and hydrophobic character causes an increase in the free energy of the system so the surfactant monomers are directed toward the interface at lower concentration so Γ_{max} decreases. By increasing the chain length of the prepared double tailed cationic surfactant, the rate of surfactants monomer migration to surface increases because of increasing hydrophobicity, and so the packing densities of prepared double tailed surfactants at the interface decreased. This force the organization of surfactant molecules to be less perpendiculars, in addition the long chain of the tail with head group less rigid, make it more prone to the coil, so the average minimum surface area decreases [23,42].

3.6. Micellization and adsorption thermodynamic study

The adsorption and micellization thermodynamic parameters of prepared double tailed aminoamine cationic surfactant have been calculated by using the CMC values obtained from surface tension measurements and α values from conductometry measurements using Gibb's adsorption equation [42]:

$$\Delta G^{o}_{mic} = (2 - \alpha)\ RT \ln(CMC)$$

$$\Delta G^{o}_{ads} = \Delta G^{o}_{mic} - (\pi_{CMC}/\Gamma_{max})$$

$$\Delta S_{mic} = -d\ (\Delta G^{0}_{mic}/\Delta T)$$

$$\Delta S_{ads} = -d\ (\Delta G^{o}_{ads}/\Delta T)$$

$$\Delta H_{mic} = \Delta G^{o}_{mic} + T\,\Delta S_{mic}$$

$$\Delta H_{ads} = \Delta G^{o}_{ads} + T\,\Delta S_{ads}$$

The micellization and adsorption behaviors of the prepared double tailed surfactant in aqueous medium were studied at three different temperatures 25, 40 and 60 °C. The change in the free energy of micellization ΔG^{o}_{mic} and adsorption ΔG^{o}_{ads} were listed in Table 2. Both values are negative indicating that the two processes are spontaneous; in another mean the migration of surfactant monomers from bulk to be adsorbed at air–water interface or aggregate in clusters forming micelle is favorable where the energy of adsorbed or micellized form is lower than surfactant monomers in bulk [43–45]. From the data in Table 2, we note that the change in free energy of both adsorption and micellization processes increases in negative direction by increasing both the chain length of double tailed cationic surfactants and temperature of the system. This could be explained according to the following:

(a) increasing the chain length of prepared aminoamine surfactants was accompanied by increasing the hydrophobicity of the aqueous system in which the surfactant can be dissolved. In addition the amphipathic structure of surfactants will lead to destroying the water structure thus increasing the free energy of the system, so the surfactant monomers migrate to the surface where the tail can be in contact with air, and/or these monomers aggregate in clusters where the tail can be interior to the micelle while the

Table 3
Antimicrobial activity of synthesized surfactants against pathogenic bacteria and fungi.

Microorganism	Gram reaction	Inhibition zone diameter (mm/mg sample)			Used standard reference	Ref. inhibition zone diameter (mm/mg sample)
		I	II	III		
Bacillus subtilis	G^+	15	15	10	Ampicillin	20
Escherichia coli	G^-	15	16	10	Ampicillin	22
Pseudomonas aeruginosa	G^-	14	14	9	Ampicillin	17
Staphylococcus aureus	G^+	16	14	10	Ampicillin	18
Aspergillus flavus	Fungus	0.0	0.0	0.0	Amphotericin B	17
Candida albicans	Fungus	0.0	0.0	0.0	Amphotericin B	19

Table 4
Biocidel effect of the prepared compounds against sulfate reducing bacteria, SRB.

Compound	Conc.			
	$1*10^{-3}$ (M)	$1*10^{-4}$ (M)	$5*10^{-5}$ (M)	$1*10^{-5}$ (M)
Blank	10^7			
I	10	10^2	10^3	10^3
II	10^2	10^3	10^3	10^3
III	10^3	10^3	10^3	10^3

cationic head be in contact with polar medium. The previous two behaviors decrease the energy of the system, so the change in the free energy of the prepared surfactant-solvent system will be decreased and increased in the negative direction.

(b) Increasing the temperature of surfactant aqueous system causes a decrease of hydration around the hydrophilic group, so the hydrophobicity of the system increases and accompanied by increasing the energy of the system, so molecules of surfactant tend to adsorb and form micelle to decrease the energy of the system.

By comparing ΔG^{o}_{mic} and ΔG^{o}_{ads} in Table 2, we note that the change in the free energy of adsorption at certain temperature higher than the change in free energy of micellization which indicate that the prepared amidoamine double-tailed cationic surfactants favor adsorption at air–water interface first till maximum surface saturation then the monomers in bulk aggregates in clusters. The change in the entropy of both micellization ΔS_{mic} and adsorption ΔS_{ads} values were listed in Table 2, and it found to be positive values indicating the disruption of water structure around the double tailed hydrocarbon when they transfer from the aqueous bulk to the air–water interface or to the micellar interior. The change in the entropy of adsorption ΔS_{ads} is more positive than that of micellization ΔS_{mic}, this reflect the greater freedom of hydrophobic part through motion to the interface than to form micelle [46–47].

3.7. Antimicrobial activity

The effect of prepared aminoamine double tailed cationic surfactants on the bacteria and fungi has been determined and recorded in Table 3, where they can be used as antibiotic against the tested bacteria (Gram positive and negative), but they don't have any effect on the tested fungi (*Aspergillus flavus* and *Candida albicans*).

The obtained result showed that the activity of prepared double tailed cationic surfactant increases by increasing the length of the hydrophobic tail till maximum inhibition efficiency at chain length of twelve carbon atom (II), then it decreases again at sixteen carbon atom chain length (III), this behavior is known by cut-off effect [48–50].

There are some parameters effect on that phenomenon like, critical micelle concentration of the used surfactant antibiotic, the change in the free energy of adsorption on the cell membrane of bacteria, and the size of diffused surfactant and the hydrophobicity of surfactant. The net effect is the magnitude of all the previous parameters. Increasing the chain length accompanied by decreasing the CMC, and so the concentration at surface be lower, consequently the activity of I > II > III, at the same time increasing the hydrophobic character, the rate of adsorption at membrane interface be higher as discussed previously, so it predicted that III > II > I. Other theory return the cut-off effect to a decrease in the perturbation of the membrane at higher alkyl tail, assuming that the longer chain, the better mimic molecule in the lipid layer, leading to disruption in the membrane. From the data recorded in Table 3, it was found that the prepared double tailed cationic surfactants with tail of twelve carbon atom has the maximum effect on Gram positive and Gram negative bacteria [51–54].

Sulfate reducing bacteria (SRB) is one of the sources of H_2S, which increases the corrosiveness of brine and causing metals to crack and blister especially in petroleum industry. The strategies to mitigate and control the microbial induced corrosion by SRB in the petroleum company are to use biocide capable of reducing the growth of this type of bacteria. The prepared double tailed surfactants have been tested against sulfate reducing bacteria, using the serial dilution technique, the contaminated water by SRB were supplied from AGIBA petroleum company and subject to growth to 107 bacteria cell/ml. The obtained results were listed in Table 4, where the prepared surfactants have good activity and can suppress the growth of bacteria and the prepared surfactants I, was found to have maximum efficiency as shown in Table 4.

The structure of bacteria cytoplasmic membrane of Gram-positive and Gram-negative bacteria is shown in Fig. 9. The main composition of the membrane is phospholipid and protein. The phosphatidylethanolamine (almost neutral at physiological pH) is a major component present in the bacterial cytoplasmic membrane and that phosphatidylglycerol

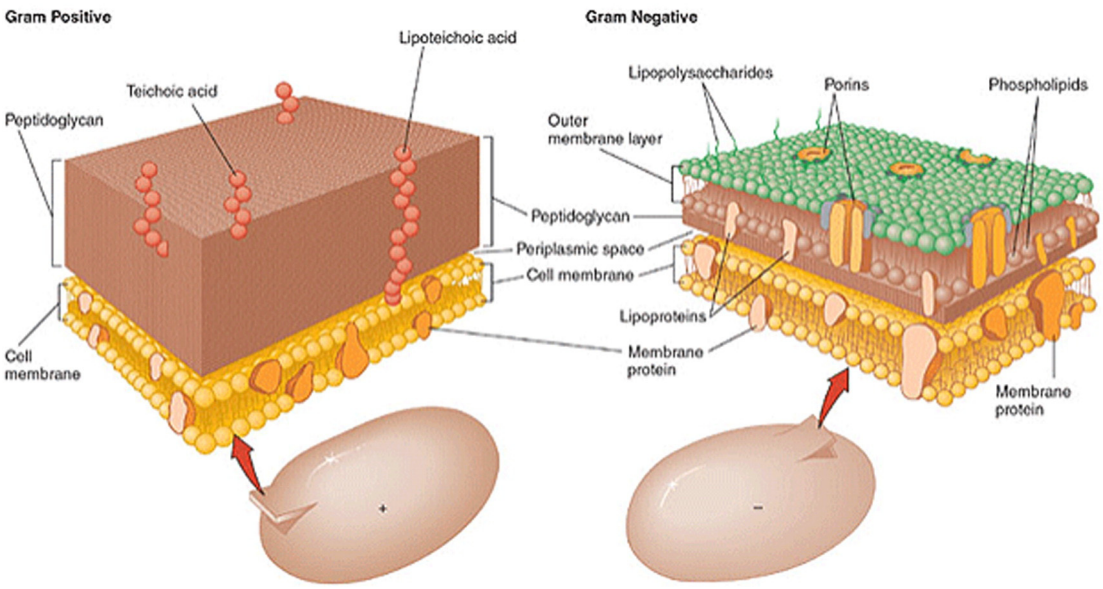


Fig. 9. Structure of the bacterial cell walls.

and its dimer, cardiolipin (both of which are negatively charged at physiological pH), are major acidic components. The predicted mechanism of prepared aminoamine double-tailed cationic surfactants as antibiotic can be explained on their adsorption ability on the cellular cytoplasmic membrane. The prepared surfactant can interact through their positive head group with the negatively charged membrane. At the complete surfactants coverage, the lipophilic tail can penetrate and disturb the selective permeability of the membrane and cause death for the cell, beside the effect of the counter ion (Br^-) [55–58].

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