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Adsorption and micellization behavior of synthesized amidoamine cationic surfactants and their biological activity

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ABSTRACT

The adsorption and micellization behavior at aqueous surface of synthesized amido-amine cationic surfactants was studied using surface tension and conductometric measurements at three different temperatures of 25, 40 and 60 °C. The chemical structure of the synthesized cationic surfactants was confirmed using Fourier transform infrared and proton nuclear magnetic resonance spectroscopy. The synthetic route is simple and comprises two steps. The first is amidation between palmitic acid and dimethyl amino propyl amine, while the second step is quaternization of the first step product with different alkyl bromides. The study evaluated the effect of temperature and the hydrophobic chain length of the synthesized amidoamine cationic surfactants on the studied surface parameters. In aqueous system the adsorption tendency of the synthesized cationic surfactants is higher than micellization and both increase by increasing the hydrophobic character and the solution temperatures. The synthesized surfactants were found to have good antibiotic effect against gram positive and negative bacteria and fungi.

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1. Introduction

The adsorption and micellization of surfactants at the water–air interface have an effect on the properties of the water. The adsorption of the surface-active agent on the surface reduces the surface tension, which is the major factor for wider applications of surfactants [1–7]. Adsorption is the key factor for various applications like corrosion inhibitors (increasing adsorption, the inhibition efficiency, increase) and as capping agent in nanotechnology [8–10]. The opposing two parts of surfactants are the key factor for the adsorption at interfaces and aggregates in the bulk solution. Studying the physicochemical of the synthesized surfactants at the surface is very important in determining the best application, in which they may be used. Since most surfaces and natural colloid are often negatively charged, so the cationic surfactants provide a strengthen adsorption layer [11]. There are many papers that reported the biological activity of commercially available cationic surfactants like N-alkyltrimethyl ammonium halides (CTAB, TTAB, DTAB, CTACl) [12,13] and N-alkyl pyridinium such as cetyl or dodecyl pyridinium chloride (CPCl, DPCl) [14] and alkyl dimethyl benzyl ammonium surfactants (benzalkonium and benzethonium) are other examples of commercially produced surfactants investigated and widely used as disinfectants in hospitals [15]. Commercial twin-chain surfactants, capable of forming vesicles, as dialkyl dimethyl ammonium halides (DDACl, DDAB and DODACl), were also studied [16]. In our study, we prepared cationic surfactants with twin chain and containing an amide functional group, which enhances its biodegradability, and reducing its aquatic toxicity. Intermediates produced in the degradation process of amide were found to be biodegradable and less toxic [17]. The microorganism gained self-immunity from conventional antibiotic, so the researchers focused on searching new antibiotic like surfactants. The research aimed to prepare cationic surfactant containing twin chain and amide group from the low price material. The physicochemical and thermodynamic of the aqueous solution of surfactants were determined from surface tension and conductance measurements at three different temperatures. The antibiotic effect of the synthesized cationic surfactants was determined using filter paper disk agar method against gram positive and negative bacteria and fungi.

2. Materials & experimental

2.1. Materials

Dimethylaminopropylamine, hexadecanoic acid and 1,3-dibromo propane were purchased from Sigma Aldrich Company. Decyl bromide, dodecyl bromide and hexadecyl bromide were purchased from Merck Company and used as it without any purification. All the used organic solvents were purchased from Algomhoria Chemical Company.

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2.2. Synthesis of amidoamine cationic surfactants

2.2.1. Synthesis of N-(3-(dimethylamino) propyl) palmitamide

The first step is amide formation through reaction of 0.03 mol from palmitic acid (7.7 g) with 0.1 mol from dimethylamino-1-propylamine (3.06 g) in 130 mL toluene. p-Toluene sulphonic acid (0.01%) was added as dehydrating agent to the reaction mixture. The reaction was stopped after complete removal of the reaction water (0.03 mol, 0.54 mL) using Dean–Stark system. The solvent was removed using vacuum rotary evaporator. The catalyst was extracted from the reaction medium using petroleum ether. Subsequent purification was done by means of vacuum distillation to remove the excess and residual materials [18].

2.2.2. Synthesis of N-(3-(dimethyl alkyl ammonio) propyl) palmitamide bromide derivatives

0.01 mol from the synthesized amide in the first step (3.41 g) was refluxed with 0.01 mol from the alkyl halides decyl bromide (2.21 g), dodecyl bromide (2.49 g), and hexadecyl bromide (3.05 g) separately in the presence absolute ethyl alcohol as a solvent for 25–30 h depending on the alkyl halide. After evaporating the absolute alcohol, the residual was purified with diethyl ether. The obtained product labeled DMOPP, DMDPP and DMHPP for cationic surfactant with decyl, dodecyl and hexadecyl alkyl chain respectively. The synthetic routes are represented in Scheme 1.

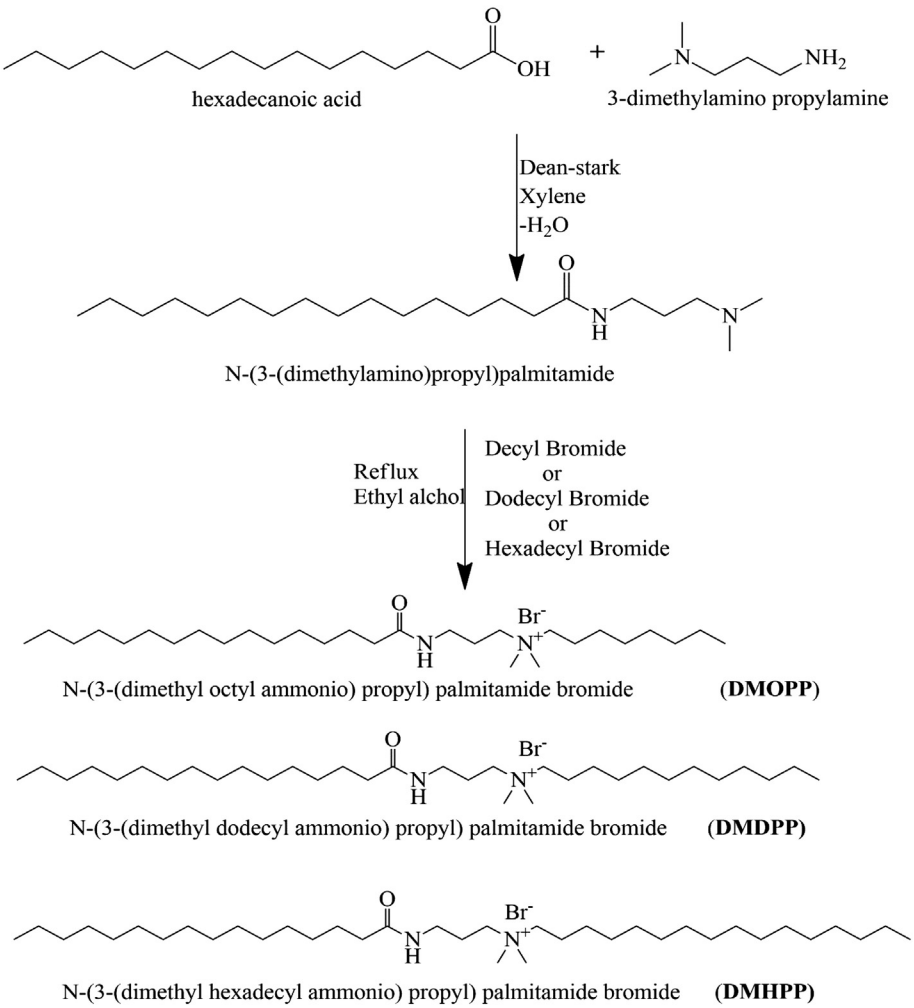
2.3. Structure confirmation

The synthetic routes of novel cationic surfactants were trappable by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}HNMR). The FTIR analysis was done in Egyptian Petroleum Research Institute using ATI Mattsonm Infinity Series™, Bench top 961 controlled by Win First™ V2.01 Software while ^{1}HNMR was done in National Research Institute using GEMINI 200 (^{1}H 200 MHz) in DMSO-d_6.

2.4. Measurements

2.4.1. Surface tension measurements (γ)

The surface tension of aqueous solution of the novel amidoamine twin chain cationic surfactant were measured by a platinum ring detachment method using a K6 Krüss (Hamburg, Germany) tensiometer at three different temperatures 25, 40 and 60 ± 0.1 °C. The accuracy of the measurements was ±0.5 mN·m−1. The platinum ring was cleaned before each measurement with diluted chromic acid mixture solution and washed with double distilled water. Each concentration was measured three times and the average was recorded and used without correction. The critical micelle concentration (CMC) was determined from the break point in surface tension (γ) versus [log c] plots [19].



Scheme 1. Synthetic route of novel cationic amidoamine surfactants.

2.4.2. Conductivity measurements

The conductivities of the studied aqueous solution of the synthesized cationic surfactants were measured at three different temperatures 25, 40 and 60 ± 0.1 °C using a digital conductivity meter Cond 3210 SET 1, Probe tetra corn 325 (Wissenschaftlich Technische Werkstattern), having a sensitivity of 1 μS cm^{-1} and an accuracy of ±0.5%. The solutions were prepared from deionized double distilled water having a conductivity of 1.9 μS cm^{-1}. The electrodes were washed, after each reading, several times with deionized water [20].

2.4.3. The biological activity evaluation

The biological activity of the synthesized double chain cationic surfactant containing the amide group was evaluated using filter paper disc agar against some pathogenic bacteria and fungi. The gram-positive bacteria were *Bacillus subtilis* and *Staphylococcus aureus* while gram-negative were *Escherichia coli* and *Pseudomonas aeruginosa*. The *Candida albicans* and *Aspergillus flavus* were used as an example for fungi. The source of the microorganism was micro analytical center, Cairo University [21]. The procedures were as follows:

1. Inoculate flask of melted agar medium with the organism to be tested.
2. Pour this inoculated medium into a petri dish.
3. After the agar has solidified, a multilobed 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 fungi).
6. Measure each clear zone and compare between them to determine the antibiotic, which is more effective.

3. Results and discussion

3.1. Structure confirmation

3.1.1. FTIR spectra

The chemical structures of the amido-amine cationic surfactants series 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 DMDPP for examples. Fig. 1 show the FTIR of DMDPP which confirm the conversion of acid to amide through disappearance the hydroxyl group of carboxylic acid which ranged from 2400 to 3400 cm^{-1} (broad band) and appearance band for amide NH at 3422.10 cm^{-1} and shifting the band of carbonyl from acid region to amide region at 1665.25 cm^{-1}. The prepared cationic surfactants show stretching vibration band of –C–H aliphatic symmetric and asymmetric at 2851.32 and 2920.17 cm^{-1} respectively in addition –CH2 bending at 1377 cm^{-1}, −CH3 bending at 1468.41 cm^{-1} and absorption band at 1255.55 cm^{-1} corresponding to C–N bond.

3.1.2. ^{1}HNMR spectra

The number and distribution of proton in the prepared amido-amine cationic surfactant were confirmed by ^{1}H-NMR spectra. Fig. 2 shows the ^{1}H-NMR spectra of N-(3-(dimethyl octyl ammonio) propyl) palmitamide bromide (DMOPP) showing signals at: δ = 0.8 (t,6H, $2CH_3$ alkyl chain); δ = 1.19 (m,34H, $-COCH_2CH_2(CH_2)_{12}CH_3$, $N^{\oplus}CH_2CH_2$ $(CH_2)_5CH_3$); δ = 1.42 (m,2H, $COCH_2CH_2(CH_2)_{12}CH_3$); δ = 1.72 (m,2H, $N^{\oplus}CH_2CH_2(CH_2)_5CH_3$); δ = 2.02 (m,2H, $N^{\oplus}CH_2CH_2CH_2NH$); δ = 2.47 (t,2H, $COCH_2CH_2(CH_2)_{12}CH_3$); δ = 2.69 (t,4H, $-CH_2N^{\oplus}(CH_3)_2CH_2-$); δ = 2.97 (t,2H, $CONHCH_2$); δ = 3.21 (s,6H, $-CH_2N^{\oplus}(CH_3)_2CH_2-$) and δ = 7.97 (m,1H, $CH_2CONHCH_2$).

3.2. Specific conductivity study

Studying the effect of chain length of the synthesized double chain cationic surfactant and the solution temperatures on the specific conductivity were clarified in Figs. 3, 4 and Table 1. Fig. 3 shows the effect of changing the alkyl chain length on the conductivity of the solution. Increasing the length of the hydrophobic chain was accompanied by a decreasing in the solution conductivity as cleared from decreasing the values of the degree of counter ion dissociation (α) recorded in Table 1. The α values of the synthesized amidoamine cationic surfactants DMOPP, DMDPP and DMHPP were 0.267, 0.254 and 0.244 at 25 °C respectively. The degree of counter ion dissociation (α) obtained using Frahm's method and equal to the ration between the postmicellar to premicellar region slops. The decreasing in conductivity (decreasing values of counter ion dissociation) with increasing chain length is a result of two factors, the number of counter ion and the strength of the bond between the counter ion and the head of the surfactant. Increasing the hydrophobic chain length of the synthesized amido-amine surfactants, the molecular weight increase so, the number of dissociated ions decrease. Also increasing the hydrophobicity of, the hydration decrease and so the charge density formed around the micelle increased so specific conductivity decreased [22–25].

Fig. 4 shows the effect of solution temperature on the specific conductivity of synthesized cationic amidoamine surfactants. The specific

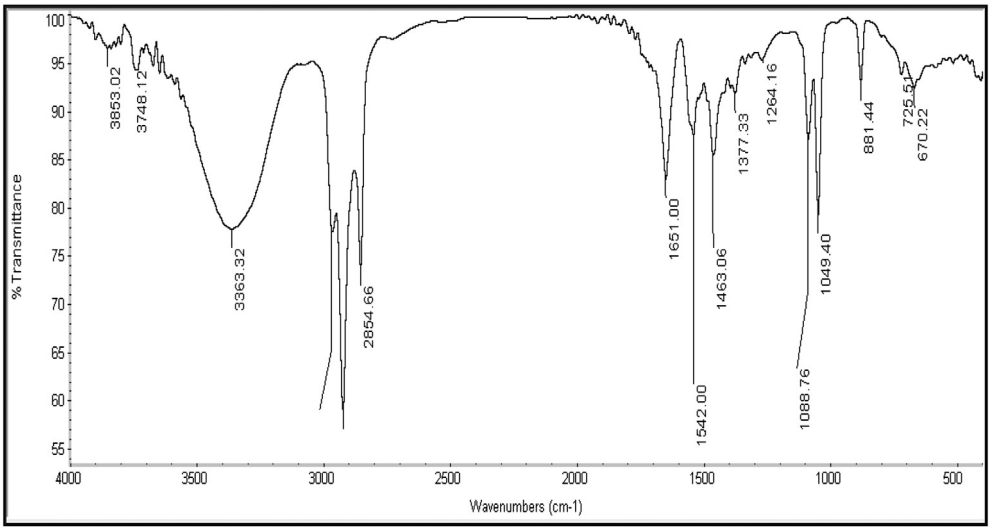


Fig. 1. IR spectrum of N-(3-(dimethyl octyl ammonio) propyl) palmitamide bromide (DMDPP).

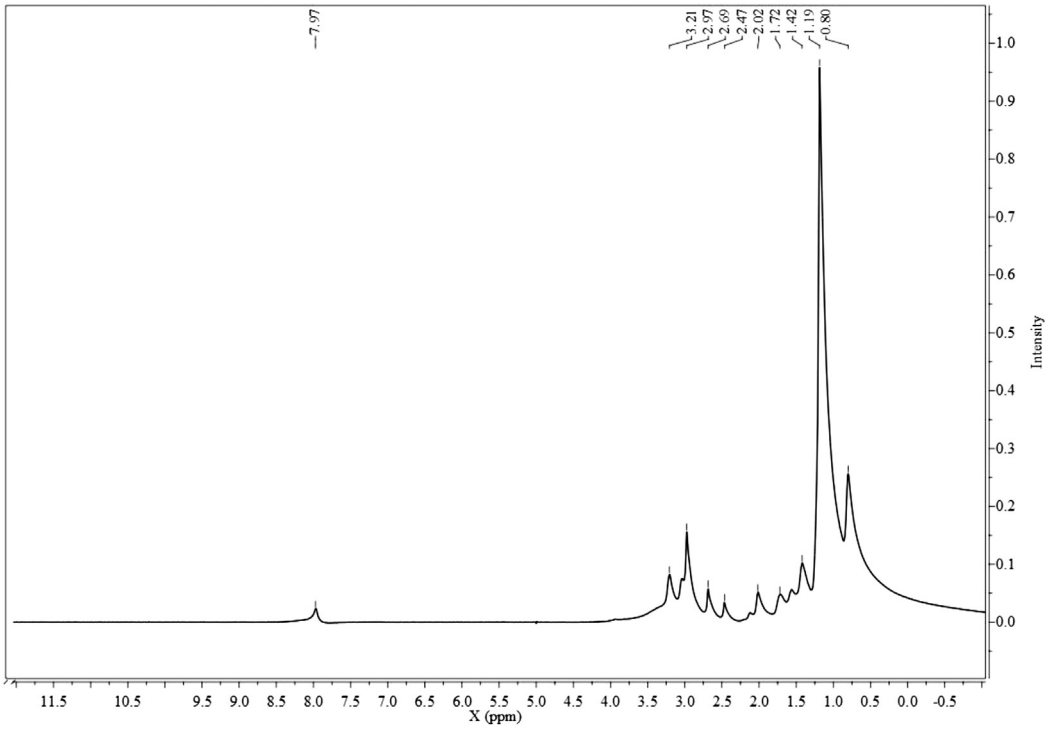


Fig. 2. ^{1}H-NMR spectrum of N-(3-(dimethyl octyl ammonio) propyl) palmitamide bromide (DMOPP).

conductivity found to increase with rising the solution temperature as indicated by increasing values of α recorded in Table 1. The degree of counter ion dissociation of an aqueous solution of DMOPP were 0.267, 0.283 and 0.3 at 25, 40 and 60 °C respectively. The behavior of conductivity with temperature return to increasing the dissociation of the counter ion from the head of synthesized double chain surfactants monomer or their micelle with rising temperature and this effect is major than the columbic attraction force between the head and its counter ion [26–29].

3.3. Critical micelle concentration (CMC) and surface activity

The critical micelle concentrations of the aqueous solution of the synthesized double chain cationic surfactants at three different temperatures 25, 40 and 60 ± 0.1 °C were determined from two different techniques; surface tension and conductivity measurements. The intersection point in Figs. 3 and 4 between the two lines which represent the relation between the specific conductivity of synthesized cationic surfactant aqueous solution and their concentration correspond to the critical micelle concentration. The abrupt change in surface tension curves represented in Figs. 5–7 refers to the CMC for the synthesized double chain surfactants at specified temperature. The calculated critical micelle concentration from the two techniques were recorded in Table 1 and they were found nearly similar but the CMC obtained from conductance measurements are higher than that obtained from surface tension due to premicellar region [30–32].

The increasing chain length of the synthesized double chain cationic surfactant has a decreasing effect on their critical micelle concentration as appeared in the data recorded in Table 1 and shown in Fig. 8. The critical micelle concentrations of aqueous solution of DMOPP, DMDPP and DMHPP were 1.806, 1.0 and 0.651 mM/L at 25 °C respectively.

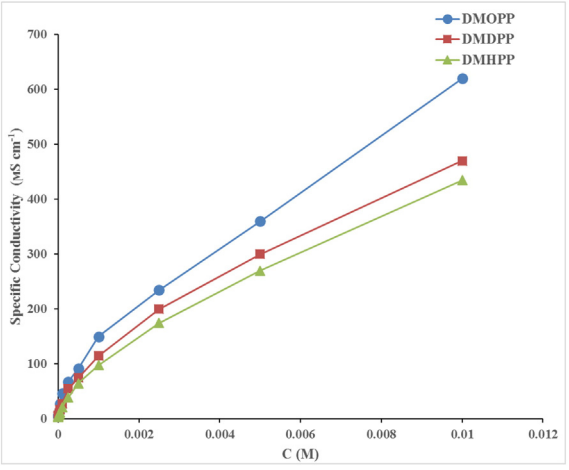


Fig. 3. The plots of specific conductivity against concentrations of the prepared cationic surfactants in distilled water at 60 °C.

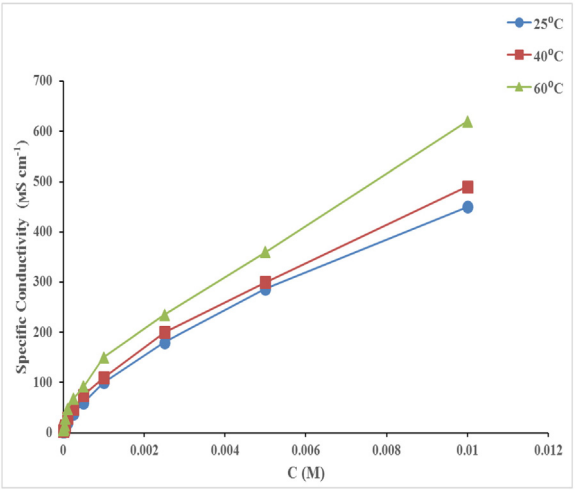


Fig. 4. The plots of specific conductivity against concentrations of the prepared cationic surfactants (DMOPP) in distilled water at 25, 40 and 60 °C.

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

Comp.	Temp. °C	CMC[a]/(mM·L^{-1})	CMC[b]/(mM·L^{-1})	α	$C_{20} * 10^{-5}$ (mol·L^{-1})	π_{CMC}/(mN·m−1)	$\Gamma_{max} * 10^{-10}$ (mol·cm^{-2})	A_{min}/A^2	CMC/C_{20}
DMOPP	25	1.806	1.810	0.267	2.512	37.91	1.62	102.52	71.90
	40	1.168	1.233	0.283	1.318	39.50	1.50	110.53	88.63
	60	0.759	0.863	0.300	0.858	37.00	1.33	124.90	88.44
DMDPP	25	1.0	1.200	0.254	1.278	39.85	1.55	107.13	78.22
	40	0.713	0.847	0.269	0.782	40.75	1.42	116.64	91.20
	60	0.464	0.621	0.274	0.558	38.00	1.32	126.17	83.18
DMHPP	25	0.651	0.803	0.244	1.000	35.23	1.35	123.32	65.06
	40	0.331	0.479	0.257	0.423	37.50	1.21	136.82	78.22
	60	0.215	0.289	0.265	0.273	35.80	1.09	152.93	78.80

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

Increasing the hydrophobicity of the synthesized cationic surfactants, lead to increasing the free energy of the aqueous system and so the surfactant monomers aggregate into clusters. In clusters the hydrophobic tail becomes interior the clusters to avoid energically unfavorable contact with aqueous medium, while the hydrophilic head becomes in contact with aqueous medium, thus the free energy of the system decreased and consequently CMC decrease [33–35].

In micelle formation, the hydration around the hydrophilic head increase compared to unimers which observed by an abrupt increase in conductivity as in Figs. 3 and 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 be formed in the bulk not surface.

Elevating the aqueous solution temperature, the critical micelle concentration decrease in as shown in Fig. 8 and Table 1. The CMC of the synthesized double chain cationic surfactant DMOPP were 1.806, 1.168 and 0.759 mM/L at 25, 40 and 60 °C respectively. The temperature has two opposing effects, decreasing the hydration around the hydrophilic head which enhance micelle formation. The second effect is disrupting the water structure around the hydrophobic tail by which the surfactants disfavor micellization, therefore the net effect is the magnitude of the two opposing effects. From the obtained data in Table 1, the predominant effect decreasing the hydration around the hydrophilic head group, hence CMC decreased [36–38].

The critical micelle concentration of the synthesized amidoamine surfactants showed higher critical micelle concentration than CMC of Gemini surfactant with the similar number of carbon atoms prepared by S.M. Shaban et al. [39]. The CMC of DMHPP at 25 °C was 0.651 mM/L while it was 0.327 mM/L for the surfactants C16-S3-C16 [39]. This can be attributed to increasing the hydrophobicity by the spacer [40].

The effectiveness of synthesized double tailed cationic surfactants (π_{CMC}) in reduction of the surface tension has been determined from surface tension measurements using the following equation:

$$\boldsymbol{\pi_{CMC}=\gamma_o - \gamma_{CMC}} \quad (1)$$

The effectiveness is the difference in the values of surface tension at the critical micelle concentration ($\boldsymbol{\gamma_{CMC}}$) and at blank water without surfactants (γ_o). The calculated (π_{CMC}) values were recorded in Table 1. The best effective surfactant is one, which has a higher ability to reduce the surface tension that has higher CMC/C_{20} value. By inspection data in Table 1, it is clear that increasing the chain length of synthesized double chain cationic surfactant, the values of CMC/C_{20} increase then it decreased at the surfactants with higher chain length (DMHPP). So the synthesized double chain amidoamine cationic surfactant DMDPP is the most effective one in the reduction the surface tension where it has the larger CMC/C_{20} which equal to 78.22, 91.2 and 83.18 at 25, 40 and 60 °C respectively. The higher value of effectiveness is indicative of the condensed nature of synthesized double tailed surfactants unimers at the aqueous medium/air interface and the lower value refer to that the formed monolayer from the monomers is more expanded [41–43].

The efficiency of the specific surfactant (C_{20}) is the concentration of the surfactant required to suppress the surface tension of the blank solution by 20 dyne/cm. The values of efficiency were calculated from surface tension measurements and recorded in Table 1. By analyzing these data, we noted that the efficiency of synthesized double tailed cationic surfactant increase by elevating both temperature and the hydrophobicity. By rising the temperature of the synthesized surfactants aqueous solution from 25 to 60 °C, the decreasing hydration around the hydrophilic head of surfactants unimers is the predominant effect, so the rate of migration of the surfactant unimers to surface increase

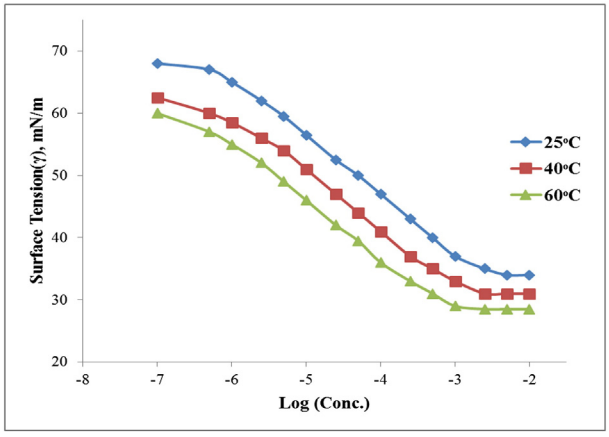


Fig. 5. The relation between surface tension and log concentration of cationic surfactant (DMOPP) at various temperatures.

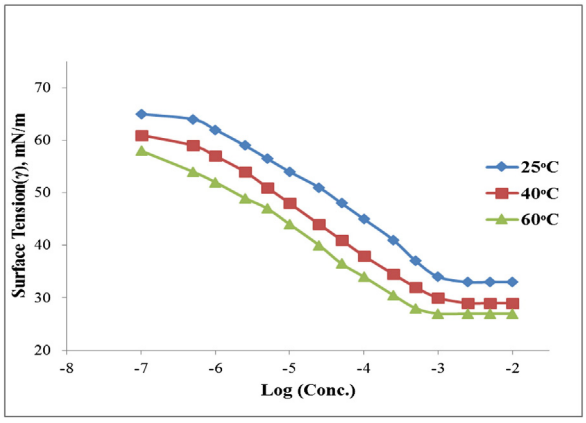


Fig. 6. The relation between surface tension and log concentration of prepared cationic surfactant (DMDPP) at various temperatures.

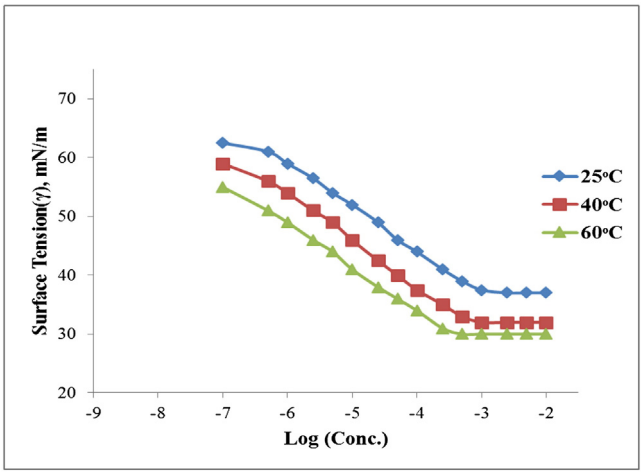


Fig. 7. The relation between the surface tension and log concentration of prepared cationic surfactant (DMHPP) at various temperatures.

so more reduction at surface tension. Increasing the hydrophobic tail chain length, the hydrophobicity increase, hence the adsorption at surface increase is being at more lower concentration [44–46].

The surface excess of synthesized cationic surfactants is expressed as the concentration of synthesized surfactant unimers at the interface per unit area. The values of maximum surface excess Γ_{max} calculated using Gibb's adsorption equation from surface tension measurements [47].

$$\boldsymbol{\Gamma_{max}} = -\,(\mathbf{1/2.303\ nRT})\,(\delta\,\boldsymbol{\gamma}/\delta\,\mathbf{logc})_{T} \tag{2}$$

where R is the gas constant, n is the number of active species (n equal 2 for cationic surfactant with monovalent counter ion), ($\delta\,\gamma/\delta\log c$) is the surface pressure and T is the absolute temperature.

Minimum average surface area is the average area (in square angstrom) occupied by each cationic unimer adsorbed at the system interface. A_{min} values give information about the orientation of the prepared surfactant at the interface [48]. The minimum surface area (A_{min}) calculated from Gibb's adsorption equation:

$$\boldsymbol{A_{min}} = \mathbf{10^{16}}/\boldsymbol{\Gamma_{max}}\,\mathbf{N} \tag{3}$$

where N is Avogadro's number. The calculated maximum surface excess and minimum surface area of the synthesized cationic surfactant at three different temperatures 25, 40 and 60 °C were recorded in Table 1, by analyzing these data it was found that the both parameters are found to depend on solution temperature and the hydrophobic chain length of synthesized cationic surfactant. Rising the solution temperature and increasing the hydrophobicity leading to increasing the free energy of the system and enhance the unimers of the synthesized cationic surfactants to migrate to the surface more rapidly at lower concentration so the packing densities of prepared cationic surfactants at the interface decreased Γ_{max} decrease. The dense packing of cationic unimers force them to be less perpendicular [49,50].

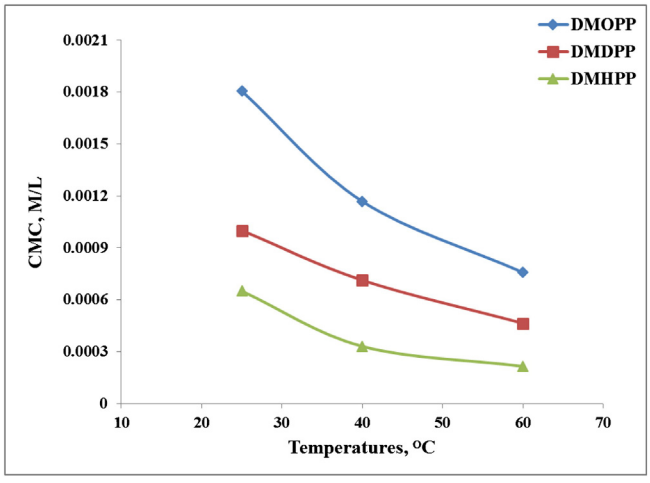


Fig. 8. Temperatures & hydrophobic chain length effect of synthesized cationic surfactant on critical micelle concentration values of prepared cationic surfactants.

The maximum surface excess of the synthesized amidoamine surfactants are higher than that in Gemini surfactant with similar number of carbon atoms prepared by S.M. shaban etals [39]. The $\boldsymbol{\Gamma_{max}}$ of DMHPP at 25 °C was 1.35×10^{-10} mol/cm^2 while it was 0.43×10^{-10} mol/cm^2 for the surfactants C16-S3-C16 [39]. From which we can conclude that the synthesized double-tailed surfactants have higher ability to accumulate at surface with more tightly packed and coherent interfacial films. Hence, the synthesized surfactants can show higher activity as emulsifier, foaming, corrosion inhibitors and phase transfer catalyst [40].

3.4. Micellization and adsorption thermodynamic study

The adsorption and micellization behavior of the prepared cationic surfactants in aqueous medium were clarified from their thermodynamic properties, which calculated using the model proposed by Zana [51].

$$\Delta G^{\circ}_{mic} = (2-\alpha)\,RT\ln(X_{CMC}) \tag{4}$$

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{mic} - (\pi_{CMC}/\Gamma_{max}) \tag{5}$$

$$\Delta S_{mic} = -\,d\,(\Delta G^{\circ}_{mic}/\Delta T) \tag{6}$$

$$\Delta S_{ads} = -\,d\,(\Delta G^{\circ}_{ads}/\Delta T) \tag{7}$$

$$\Delta H_{mic} = \Delta G^{\circ}_{mic} + T\,\Delta S_{mic} \tag{8}$$

$$\Delta H_{ads} = \Delta G^{\circ}_{ads} + T\,\Delta S_{ads}. \tag{9}$$

The degree of counter ion dissociation was obtained from conductance measurement while π_{CMC}, Γ_{max} and CMC were determined from surface tension measurements. The calculated thermodynamic parameters were recorded in Table 2. The data in Table 2 demonstrate that the change in the free energy of adsorption and micellization are negative at all the tested temperatures, which indicate that the two processes are spontaneous. The change in free energy of micellization of the synthesized cationic surfactants DMOPP are −44.39, −48.08 and −52.65 kJ mol^{-1} at 25, 40 and 60 °C respectively. By rising the aqueous solution temperatures, the change in the free energy of micellization increase in the negative direction indicating that micellization is favorable with elevating the temperature. The change in the free energy of adsorption of the synthesized cationic surfactant increase in the negative direction by elevating temperature; for example ΔG^{o}_{ads} were −46.73, −50.71 and −55.44 kJ mol^{-1} for the synthesized DMOPP at 25, 40 and 60 °C respectively. Elevating the temperature of the surfactant aqueous system cause a decrease of hydration around the hydrophilic group, so the hydrophobicity of the system increase 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 [52–54].

By increasing the hydrophobic character of synthesized double chain cationic surfactants, the change in the free energy of micellization and adsorption increase in the negative direction, for example the change in free energy of micellization ΔG^{o}_{mic} were −48.08, −50.72 and −54.54 for the synthesized DMOPP, DMDPP and DMHPP

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

Comp	Temp. °C	ΔG°_{mic} kJ·mol^{-1}	ΔH_{mic} kJ·mol^{-1}	ΔS_{mic} kJ·mol^{-1}·K^{-1}	ΔG°_{ads} kJ·mol^{-1}	ΔH_{ads} kJ·mol^{-1}	ΔS_{ads} kJ·mol^{-1}·K^{-1}
DMOPP	25	−44.39	–	–	−46.73	–	–
	40	−48.08	28.99	0.246	−50.71	32.40	0.265
	60	−52.65	23.48	0.228	−55.44	23.26	0.236
DMDPP	25	−47.27	–	–	−49.84	–	–
	40	−50.72	21.34	0.230	−53.58	24.56	0.249
	60	−55.81	29.04	0.255	−58.70	26.56	0.256
DMHPP	25	−49.42	–	–	−52.03	–	–
	40	−54.54	52.56	0.342	−57.64	59.36	0.374
	60	−59.77	27.31	0.261	−63.07	27.47	0.272

respectively at solution temperature 40 °C. Increasing the chain length of prepared amidoamine cationic surfactants were accompanied by increasing the hydrophobicity of the aqueous system in which the surfactant be dissolved in addition the amphipathic structure of synthesized surfactants which will lead to the destroying the water structure thus increasing the free energy of the system. Therefore, the surfactant monomers migrate to surface or aggregate in clusters. The migration to surface or aggregation in cluster decreases 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. By comparing the change in the free energy of micellization and adsorption, we note that ΔG^{o}_{ads} is more negative than ΔG^{o}_{mic} at the same temperature and chain length indicating that adsorption process is more favorable than micellization process. From that, we conclude that the synthesized cationic surfactants tend to adsorb at air-water interface first until maximum surface saturation then the monomers aggregates in bulk in cluster forms [55–57].

The change in the entropy of both micellization ΔS_{mic} and adsorption ΔS_{ads} values were recorded in Table 2, and it found to be positive values indicating the disruption of water structure around the tail of synthesized surfactant 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 [58,59].

3.5. Antimicrobial activity

The activity of the synthesized cationic surfactants containing amide group against some gram positive and negative bacteria and fungi has been recorded in Table 3. The synthesized surfactants have good activity against both tested bacteria and fungi. The antibiotic activity was hydrophobic alkyl chain dependent, where the activity increase by increasing the length of alkyl chain then, it decreases, this effect known by the cut-off effect [58–60]. Regarding to the tested bacteria the synthesized DMDPP has the maximum activity then, it decreases at surfactant with sixteen-carbon atom (DMHPP). Regarding to the fungi, the synthesized cationic surfactant with eight carbon atom chain length (DMOPP) is the most effective one that DMDPP and DMHPP.

There are some parameters, which responsible for the cut-off effect critical micelle concentration (CMC) of the synthesized cationic surfactant, the change in the free energy of adsorption ΔG^{o}_{ads} at the bacteria cell membrane, the size of diffused surfactant unimers and their micelle and the hydrophobicity of surfactant [61–64]. Increasing the chain length of the hydrophobic tail accompanied by a decreasing in the CMC as previously discussed, hence the concentration at the membrane surface become lower, consequently the activity of DMOPP > DMDPP > DMHPP. At the same time increasing the hydrophobic character, the adsorption rate at the cell membrane be higher, so it predicted that DMHPP > DMDPP > DMOPP. Another theory returns the cut-off effect to a decrease in the perturbation of the membrane at higher alkyl tail, assuming that the longer the chain, the better mimic molecule in the lipid layer, leading to disruption in the membrane. Hence the magnitude of these effects determines the most effective surfactant, from the data recorded in Table 3, it was found that the synthesized cationic surfactants with twelve carbon atoms (DMDPP) has the maximum antibiotic effect against the tested bacteria, the surfactant DMOPP has the best effect against the tested fungi.

The biological activity of the synthesized cationic surfactants is slight lower than that of Gemini surfactants with similar number of carbon atoms prepared by S.M. Shaban et al. [39]. For example the inhibiting effect of DMHPP against *B. subtilis*, *E. coli* and *S. aureus* was 12, 12 and 13 mm/mg while it was 13, 14 and 14 mm/mg for the gemini surfactant C16-S3-C16 [39], respectively. This can be attributed to that gemini surfactants contains additional counter ions and positive charge which enhance the adsorption at the cell membrane and disruption the selective permeability of the membrane.

Fig. 9 shows the main composition of Gram-positive and Gram-negative bacteria membrane. The expected mechanism of synthesized cationic surfactant as the antibiotic is based on the affinity of the surfactants to adsorb on the cellular cytoplasmic membrane and interaction between the positive head group of surfactants and negatively charged membrane where the hydrophobic tail penetrates and disturb the selective permeability of the membrane causing cell death in addition the counter ion effect [65–70].

Table 3
The antibiotic effect of synthesized gemini 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)
		DMOPP	DMDPP	DMHPP		
Bacillus subtilis	G^{+}	12	14	12	Ampicillin	20
Escherichia coli	G^{-}	13	15	12	Ampicillin	22
Pseudomonas aeruginosa	G^{-}	13	13	12	Ampicillin	17
Staphylococcus aureus	G^{+}	14	15	13	Ampicillin	18
Aspergillus flavus	Fungus	12	10	8	Amphotericin B	17
Candida albicans	Fungus	14	11	10	Amphotericin B	19

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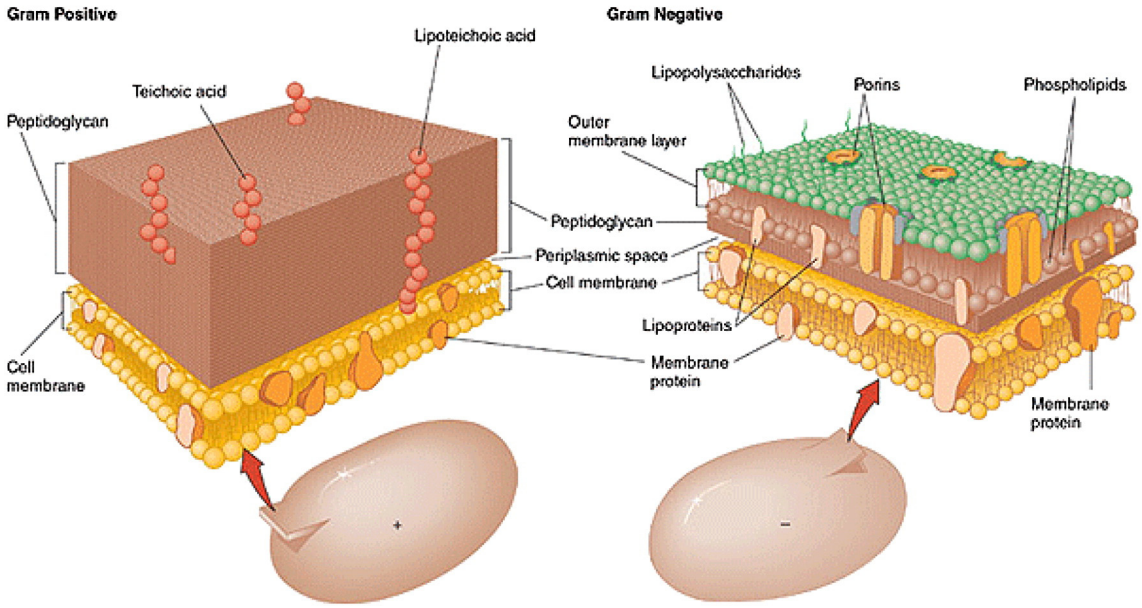

Fig. 9. The bacterial cell wall structure.

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