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Amidoamine Gemini surfactants based dimethylamino propyl amine: Preparation, characterization and evaluation as biocide

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ABSTRACT

The chemical structures of three prepared amidoamine Gemini surfactant were confirmed using FTIR and ^{1}HNMR spectroscopic methods. The synthetic routes passed through two steps, the first one is the formation of the amide and the second one is the quaternization of the prepared amide with dibromo propane. The surface and thermodynamic parameters were determined from surface tension and conductivity measurements. The obtained critical micelle concentrations from both techniques are similar. The values of CMC were found to depend on both solution temperature and hydrophobic character. The change in free energy of micellization and adsorption showed a tendency of synthesized Gemini surfactants to adsorb at the interface first then forming micelle in the bulk. The prepared Gemini surfactants act as good antibiotic against some tested bacteria and fungi.

1. Introduction

Gemini surfactants as monomeric surfactants contain two opposing parts hydrophilic and lipophilic, this amphipathic structure governs in the ability of surfactants to adsorb at interfaces and aggregate in the micelles form of higher concentration. The role of surfactant in various applications either industrial or medicinal or research arises from that amphipathic structure. In the recent years the surfactants have a very important role in nanotechnology where it participates in the nanoparticle synthesis process and also used as capping agent in other meaning preventing the aggregation of the prepared nanoparticles [1–4]. Due to the tendency of surfactant to adsorb on interface, it is used in many applications in industry like corrosion inhibitors, detergents, paints, drilling mud, petroleum recovery and others [5–9]. Gemini surfactants structured from two identical hydrophobic tails are connected together by a spacer carrying two positive charges. Because of this unique structure of Gemini surfactants, they have much lower critical micelle concentration and higher efficiency in surface tension reduction than those monomeric surfactants with similar structure [10]. The microorganism gained self-immunity from conventional antibiotic, so the research articles around the world focused on searching new categories from antibiotic like surfactants. The literature survey around Gemini surfactants reveals much study around the physiochemical and thermodynamic behavior [11–13], and lowers the focus on the behavior of Gemini surfactants as antibacterial and antifungal. The research aimed to prepare novel Gemini surfactants with low cost of commercial materials containing amide group. The chemical structure of the prepared Gemini surfactants was confirmed using different spectroscopic techniques. The critical micelle concentration was determined using surface tension and conductivity measurements. The surface parameters of Gemini surfactant determined from surface tension data at three different temperatures. The thermodynamic parameters were determined from both surface tension and conductivity. The synthesized Gemini surfactants evaluated as antibacterial and antifungal.

2. Materials & experimental

2.1. Materials

Dimethylaminopropylamine, octanoic acid, dodecanoic acid, hexadecanoic acid and 1,3-dibromo propane all purchased from Sigma Aldrich Company and were used in the synthesis of amido-amine Gemini surfactants. All the used organic solvents were purchased from Alnasr Company.

2.2. Synthesis of amidoamine cationic surfactants

2.2.1. Synthesis of N-(3-(dimethylamino) propyl)alkanamide derivatives

The amide is formed by reaction equimolar from fatty acid (octanoic acid, dodecanoic acid and hexadecanoic acid) and dimethylamino-1-propylamine in 100 mL xylene. The catalyst (0.01% p-toluene sulphonic acid) was added to the reaction mixture and the reaction completed by removal of the desired water amount (0.1 mol) using Dean-Stark

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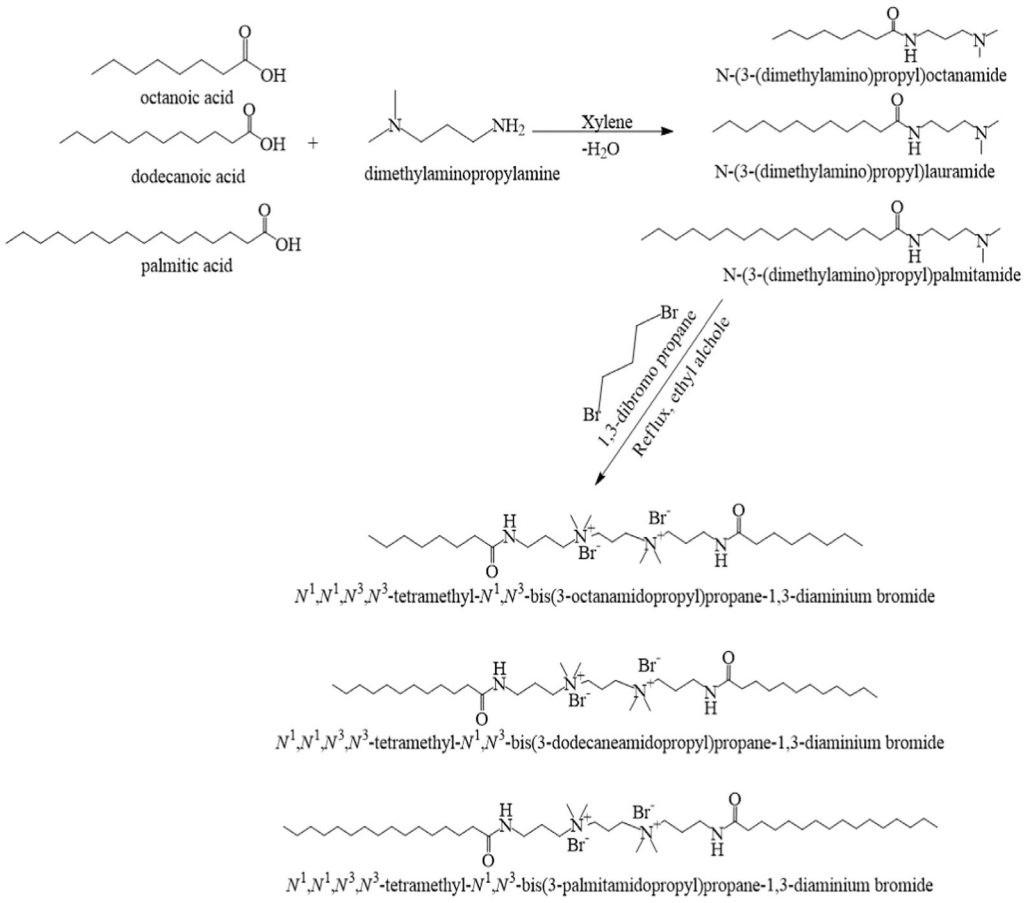

Scheme 1. Synthetic route of novel Gemini amidoamine surfactants.

system. The xylene was evaporated and the petroleum ether was used to remove the catalyst from the product [14].

2.2.2. Synthesis of Gemini surfactants

Two moles from the different fatty amides which prepared from the first step were refluxed with one mole from 1,3-dibromo propane in absolute ethyl alcohol as solvent for 25–30 h depending on hydrophobicity. After evaporating the absolute alcohol, the residual was purified with diethyl ether. The obtained Gemini surfactants labeled C8-S3-C8, C12-S3-C12 and C16-S3-C16 and the synthetic routes shown in Scheme 1.

2.3. Structure confirmation

The synthetic routes of novel Gemini surfactants were trappable by FTIR and ^{1}HNMR spectroscopy. The FTIR analysis was done in Egyptian Petroleum Research Institute using using ATI Mattsonm Infinity Series™, Bench top 961 controlled by Win First™ V2.01 Software

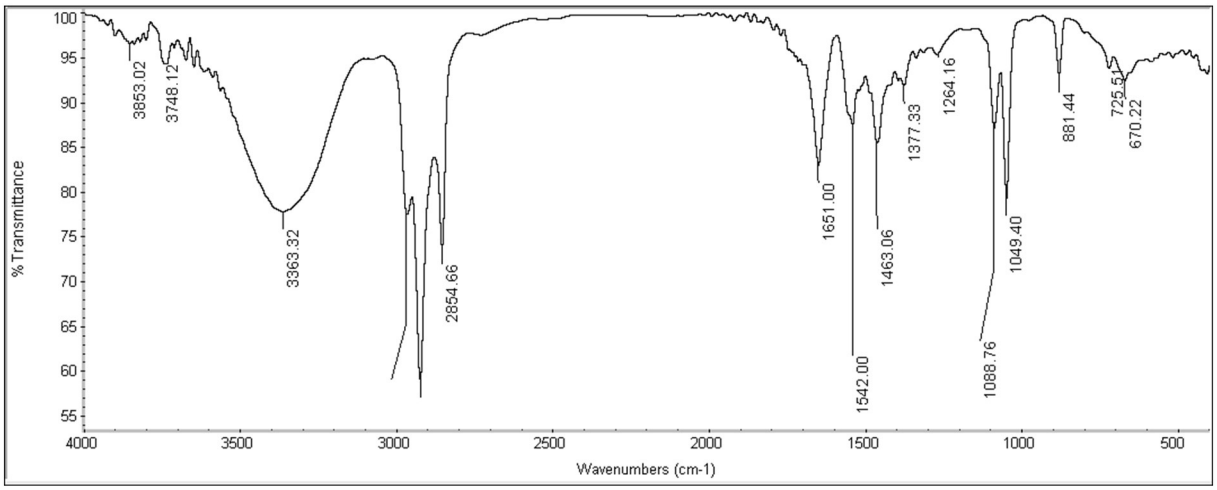

Fig. 1. IR spectrum of N^1,N^1,N^3,N^3-tetramethyl-N^1,N^3-bis(3-dodecanamidopropyl)propane-1,3-diaminium bromide (C12-S3-C12).

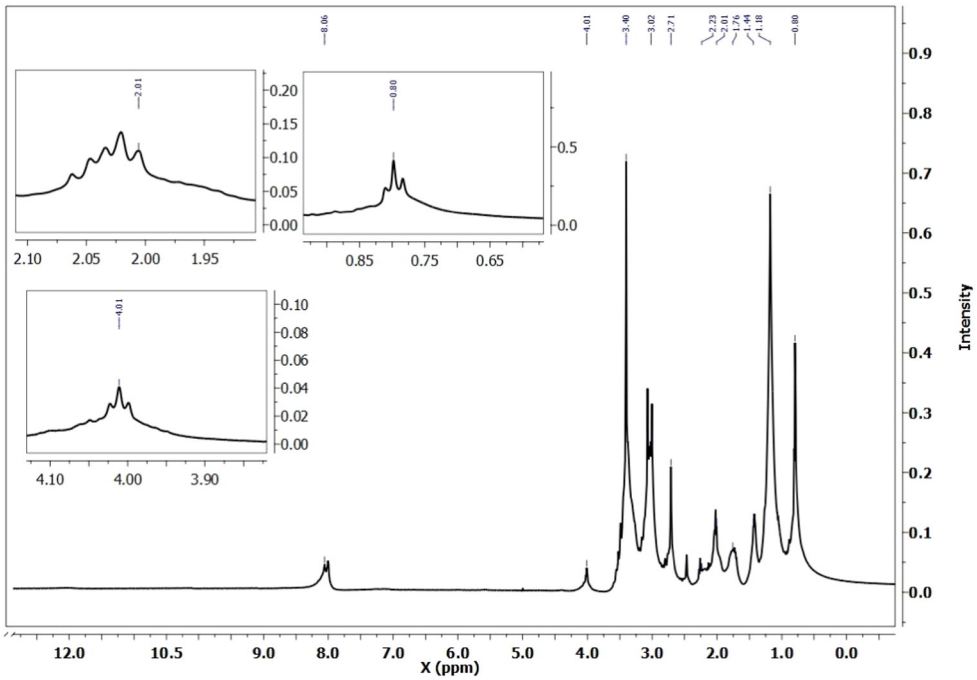

Fig. 2. ^{1}H-NMR spectrum of N^1,N^1,N^3,N^3-tetramethyl-N^1,N^3-bis(3-octanamidopropyl)propane-1,3-diaminium bromide (C8-S3-C8).

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 prepared novel Gemini surfactants at three different temperatures 25, 40 and 60 °C was measured using tensiometer-K6 Processor using the ring method (KrÜss Company, Germany). Distilled water was used before each experiment for calibration. Each concentration was repeated three times and the average was taken. The critical micelle concentrations were determined from the break point in surface tension (γ) versus [log c] plots [15].

2.4.2. Conductivity measurements

The critical micelle concentration of synthesized Gemini surfactants was also determined from conductivity measurements, which correspond to the break point in the plot of specific conductivity against concentration of specified surfactants. The conductivity was measured using Cond 3210 SET 1, Probe tetra corn 325 (Wissenschaftlich Technische Werkstattern) at the same three temperatures where surface tension measured. Water bath was used to adjust the temperature of the sample [16].

2.4.3. The biological activity of synthesized Gemini surfactants

The antibiotic activity of the prepared novel Gemini surfactants was tested against some pathogenic bacteria and fungi. The Gram-positive under test 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 micro-organism was Operation Development Center, Egyptian Petroleum Research Institute, Egypt and the filter-paper disk agar diffusion technique was used to evaluate the prepared Gemini surfactants as antibiotic. [17] The procedures were as follow:

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 disk that impregnated with different antibiotics laid on top of agar.
4. The antibiotic in each lobe of disk 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.

3. Results and discussion

3.1. Structure confirmation

3.1.1. FTIR spectra

The functional groups of the newly prepared Gemini surfactants were confirmed using FTIR spectroscopy. All the prepared Gemini surfactants have the same functional group. Fig. 1 shows the FTIR of C12-

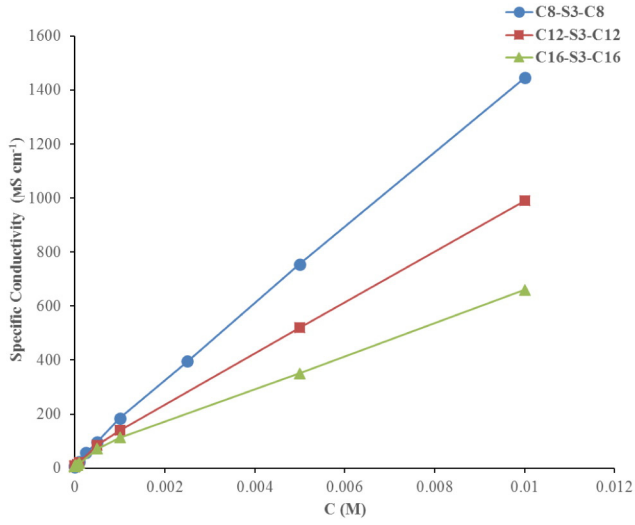

Fig. 3. The plots of specific conductivity against concentrations of the prepared Gemini surfactants in distilled water at 25 °C.

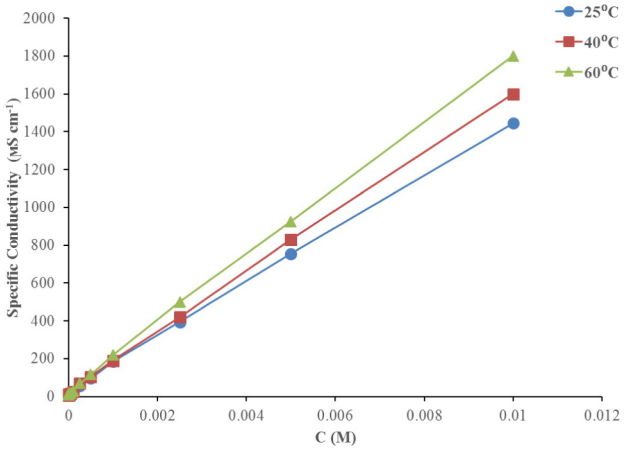

Fig. 4. The plots of specific conductivity against concentrations of the prepared Gemini surfactants (C8-S3-C8) in distilled water at 25, 40 and 60 °C.

S3-C12 Gemini surfactant which confirm the transformation 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 3291 cm^{-1} and shifting the band of carbonyl from acid region to amide region at 1649.66 cm^{-1}. The prepared Gemini surfactants show stretching vibration band of −C–H aliphatic symmetric and asymmetric at 2854.25 and 2924.29 cm^{-1} respectively in addition $-CH_2$ bending at 1376.56 cm^{-1}, $-CH_3$ bending at 1465.82 cm^{-1} and absorption band at 1063.44 cm^{-1} corresponding to C–N bond.

3.1.2. ^{1}HNMR spectra

The number and distribution of proton in the prepared amido-amine Gemini surfactant were confirmed by ^{1}H-NMR spectra. Fig. 2 show the ^{1}H-NMR spectra of N^1,N^1,N^3,N^3-tetramethyl-N^1,N^3-bis (3-octanamidopropyl) propane-1,3-diaminium bromide (C8-S3-C8), showing signals at: δ = 0.8 (t,6 H, **$2CH_3$** alkyl chain); δ = 1.18 (m,20 H, __ 2 $COCH_2CH_2$**$(CH_2)_5$**CH_3), δ = 1.44 (m,4 H, $2COCH_2$**CH_2**$(CH_2)_5(CH_3)$); δ = 1.76 (m,4 H, 2 $N^{\oplus}CH_2$**CH_2**CH_2NH); δ = 2.01 (m,4 H, 2 CO**CH_2**$CH_2(CH_2)_5CH_3$), δ = 2.23 (m,2 H, $N^{\oplus}CH_2$**CH_2**$CH_2N^{\oplus}$); δ = 2.71 (t,4 H, $N^{\oplus}$**CH_2**CH_2CH_2NH); δ = 3.02 (t,4 H, $N^{\oplus}$**CH_2**CH_2**CH_2**$N^{\oplus}$); δ = 3.40 (s,6 H, $-CH_2N^{\oplus}$**$(CH_3)_2$**CH_2-); δ = 4.01 (t,4 H, 2 $N^{\oplus}CH_2CH_2$**CH_2**NH) and δ = 8.06 (t,H, CH_2CO**NH**CH_2).

3.2. Specific conductivity of synthesized Gemini surfactants

The effect of hydrophobic chain length of synthesized Gemini surfactants and the solution temperature on the specific conductivity has been shown in Figs. (3,4) and appeared in Table 1 through the values of the degree of counter ion dissociation (α). Fig. 3 shows the effect of chain length on conductivity, where increasing chain length of synthesized Gemini surfactants decreases the specific conductivity as appeared from decreasing degree of counter ion dissociation (α) values in Table 1. The degree of counter ion dissociation (α) obtained using Frahm's method and equal to the ration between the postmicellar to premicellar region slops and was recorded in Table 1. The decreasing in α values with an increasing in chain length ascribed to a decreasing number of dissociated ions in solution with increasing the molecular weight of synthesized Gemini surfactants in addition increasing the hydrophobicity of synthesized Gemini surfactants, the hydration decrease and so the charge density formed around the micelle increased so specific conductivity decreased [18–20]. Fig. 4 shows the effect of solution temperature on the specific conductivity of synthesized Gemini amido-amine surfactants. The specific conductivity found to increase with increasing the temperature as showed by increasing values of α listed in Table 1. The behavior of conductivity with temperature ascribed to increasing the dissociation of the counter ion from the head of synthesized Gemini surfactants monomer or their micelle with elevating the solution temperature and this effect is more predominant than the columbic attraction force between the head and its counter ion [21–23].

3.3. Critical micelle concentration (CMC)

The characteristic critical micelle concentration for the prepared Gemini surfactants at the 25, 40 and 60 °C in aqueous solution were obtained from two different techniques, surface tension and conductivity. The critical micelle concentration obtained from conductive measurements through the intersection between the two lines represented in Figs. (3 & 4) between the concentration and corresponding specific conductivity. The abrupt change in the curves of surface tension represented in Figs. 5–7 refers to the CMC for the synthesized Gemini surfactants at specified temperature. The determined critical micelle concentration from both techniques were listed in Table 1, and by comparing them it was found that the two CMC are nearly similar but the CMC obtained from conductance measurements are higher than that obtained from surface tension one due to premicellar region [24–25].

As shown in Table 1 and Fig. 8 it was found that the CMC values decrease by increasing the hydrophobic chain length and solution. Increasing the hydrophobic chain length of synthesized Gemini surfactants from eight to sixteen carbon atoms, the hydrophobicity increase thus the free energy of the aqueous system will increase consequently the surfactant monomers aggregates into clusters in which the tail be interior to decrease the interaction with the polar medium thus free energy decrease, and so the CMC decreases [26,27]. In micelle formation, the hydration around the hydrophilic increase compared to monomers that observed by an 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 start 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 temperature was accompanied by a decrease in CMC as shown in Fig. 8 and Table 1, as we know; the temperature has two opposing effects, the former is decreasing the hydration around the hydrophilic head by which the surfactant

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}
C8-S3-C8	25	1.225	1.235	0.775	1.44	37.50	0.39	425.50	84.88
	40	0.582	0.644	0.794	0.67	36.26	0.35	478.91	87.33
	60	0.387	0.441	0.813	0.42	34.82	0.31	540.14	92.27
C12-S3-C12	25	0.783	0.810	0.653	0.71	42.50	0.42	396.66	110.46
	40	0.239	0.299	0.685	0.21	41.56	0.38	439.93	114.98
	60	0.123	0.150	0.717	0.10	39.00	0.32	520.87	127.66
C16-S3-C16	25	0.327	0.462	0.591	0.40	34.17	0.43	388.63	81.11
	40	0.084	0.095	0.611	0.10	35.21	0.39	430.91	83.99
	60	0.051	0.064	0.633	0.06	33.69	0.32	516.42	86.87

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

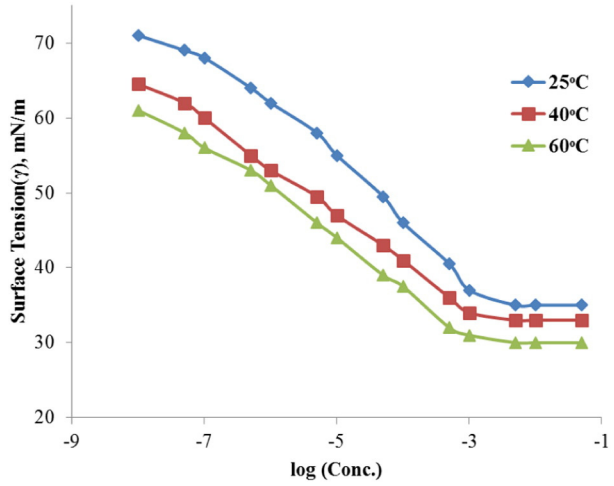

Fig. 5. The relation between surface tension and log concentration of Gemini surfactant (C8-S3-C8) at various temperatures.

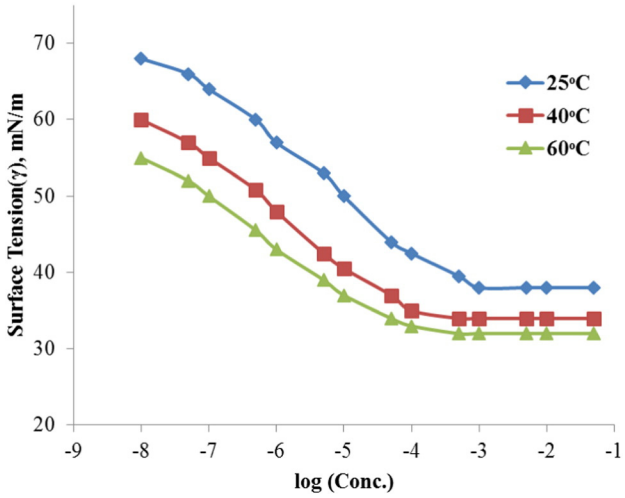

Fig. 7. The relation between the surface tension and log concentration of prepared Gemini surfactant (C8-S3-C8) at various temperatures.

favor micelle formation; while the second effect is disrupting 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 predominate effect is the former so CMC decreased [28–30].

3.4. Effectiveness and efficiency of synthesized amido-amine Gemini surfactants

The effectiveness of synthesized Gemini surfactants (π_{CMC}) to reduce the surface tension have been determined from surface tension measurements using the following equation:

$$\boldsymbol{\pi_{CMC}} = \boldsymbol{\gamma}_0 - \boldsymbol{\gamma}_{CMC}.$$

The effectiveness represents 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 obtained (π_{CMC}) values were recorded in Table 1, the most effective surfactant is that one which has a higher ability to decrease the surface tension and confirmed through values of CMC/C_{20} which listed in Table 1. The surfactant, which possess higher CMC/C_{20}, it predicts to be the highest one in reduction surface tension at critical micelle concentration. By the inspection of the data in Table 1, it reveals that by increasing the chain length of synthesized Gemini surfactant the values of CMC/C_{20} increase then decrease at the synthesized surfactants with higher chain length (C16-S3-C16 surfactant), from that we can conclude that the synthesized surfactant (C12-S3-C12) is the most effective one in reduction surface tension at CMC. The $\boldsymbol{\pi}_{CMC,}$ of C12-S3-C12 equal to 42.5 mNm^{-1} at 25 °C and has higher CMC/C_{20} equal to 110.46 at the same temperature [31–33]. The higher value of effectiveness is indicative of the condensed nature of prepared Gemini surfactants monomers at the aqueous medium/air interface and the lower value refer to that the formed monolayer from the monomers is more expanded.

The efficiency of certain surfactant (C_{20}) is the concentration of surfactant required to make a reduction in surface tension by 20 dyne/cm. The values of surfactants efficiencies were calculated from surface tension measurements and listed in Table 1. By studying these data, we noted that the efficiency of synthesized Gemini surfactant increase by elevating the temperature and increasing the hydrophobicity. By elevating the temperature, the hydration around the tail and head of synthesized Gemini surfactants monomer decreases and as discussed in the previous section the magnitude effect of elevating the temperature is decreasing the CMC. Therefore, the migration of surfactant monomers to surface is faster and at lower concentration [34,35].

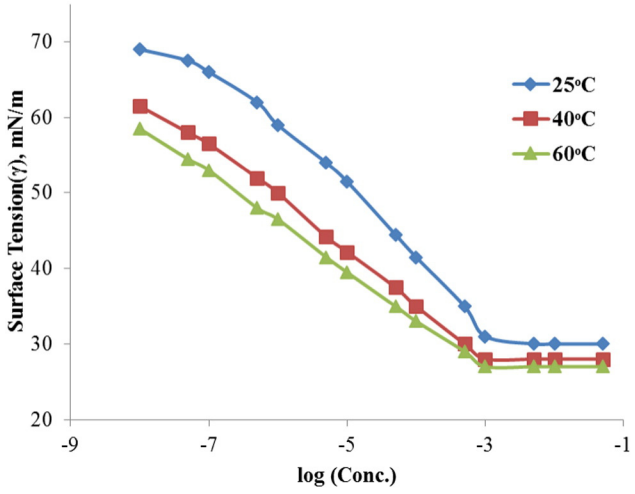

Fig. 6. The relation between surface tension and log concentration of prepared Gemini surfactant (C12-S3-C12) at various temperatures.

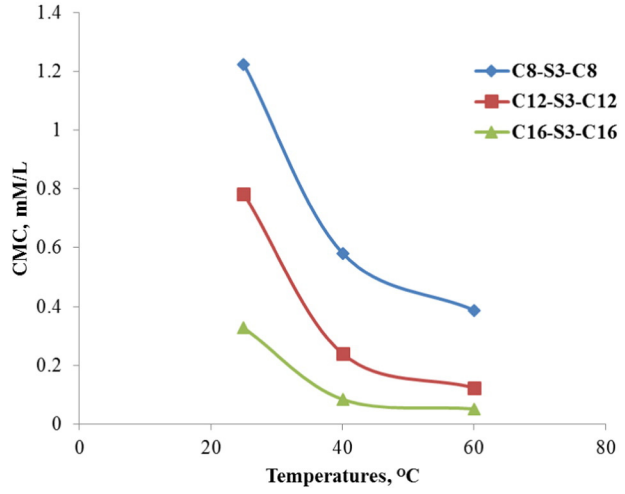

Fig. 8. Temperatures & hydrophobic chain length effect of synthesized Gemini surfactant on critical micelle concentration values of prepared cationic surfactants.

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

The surface excess of synthesized Gemini surfactants is expressed as the concentration of Gemini surfactant monomers at the interface per unit area. The values of maximum surface excess Γ_{max} calculated using Gibb's adsorption equation from surface tension measurements [36].

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

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

Minimum average surface area is the average area (in square angstrom) occupied by each Gemini monomer adsorbed at the system interface. A_{min} values give information about the angle between synthesized Gemini surfactant monomer and the interface [37].

The minimum surface area (A_{min}) of the synthesized Gemini surfactants calculated from Gibb's adsorption equation:

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

The calculated maximum surface excess and minimum surface area for synthesized Gemini surfactants at the three different temperatures 25, 40 and 60 °C were listed in Table 1. By analyzing these data it was found that both the maximum surface excess and minimum surface area depend on solution temperature and the hydrophobic chain length of synthesized Gemini cationic surfactant. Elevating the solution temperature and increasing the hydrophobic chain length lead to an increasing in the free energy of the system and enhance the monomers of the synthesized Gemini surfactants to migrate to the surface more rapidly at lower concentration so the packing densities of prepared Gemini cationic surfactants at the interface decreased consequently, the surfactant monomers concentration at interface Γ_{max} decreased. The dense packing of Gemini monomer force them to be less perpendicular so minimum surface area occupied by a surfactant monomer increase [38–39].

3.6. Micellization and adsorption thermodynamic study

The behavior of synthesized Gemini surfactants in solution was determined from their thermodynamic parameters of adsorption and micellization using pseudo-phase separation model for Gemini surfactants proposed by Zana, [40].

$$\Delta G^o_{mic} = 2(1.5-\alpha)RT\ln(X_{CMC})$$
$$\Delta G^o_{ads} = \Delta G^o_{mic} - (\pi_{CMC}/\Gamma_{Max})$$
$$\Delta S_{mic} = -d(\Delta G^o_{mic}/\Delta T)$$
$$\Delta S_{ads} = -d(\Delta G^o_{ads}/\Delta T)$$
$$\Delta H_{mic} = \Delta G^o_{mic}/T\Delta S_{mic}$$
$$\Delta H_{ads} = \Delta G^o_{ads}/T\Delta S_{ads}$$

The critical micelle concentration, maximum surface excess and effectiveness were obtained from surface tension measurements while the degree of counter ion of dissociation determined from conductance measurements. By analyzing the data in Table 2, it was found that the change in the change in the free energy of micellization and adsorption are negative which indicate that the adsorption and the micellization behavior of synthesized Gemini surfactants in the solution at the tested temperatures are spontaneous. The change in free energy of micellization alters from −38.52 to −45.1 kJ mol^{-1} for the synthesized C8-S3-C8 by changing the solution temperature from 25 to 60 °C. i.e., the change in free energy of micellization ΔG^o_{mic} increase in the negative direction by elevating the temperature indicating that process of micellization is favorable by rising the temperature. The same trend appeared with the change in free energy of adsorption ΔG^o_{ads} of synthesized Gemini surfactants for example ΔG^o_{ads} of synthesized C8-S3-C8 change from −48.13 to −56.43 kJ·mol^{-1} by increasing the temperature from 25 to 60 °C. 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 condition indicating that process of adsorption is more favorable than micellization process. By increasing the hydrophobic character of synthesized Gemini 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 were −38.52, −46.91 and −54.27 for synthesized C8-S3-C8, C12-S3-C12 and C16-S3-C16 respectively at solution temperature 25 °C. The same trend was observed in adsorption process, where ΔG^o_{ads} increase in the negative direction with increasing the chain length as indicated in Table 2. Increasing the chain length of prepared aminoamine Gemini 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. Increasing 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. On comparing ΔG^o_{ads} and ΔG^o_{mic} in Table 2, we note that the change in the free energy of adsorption ΔG^o_{ads} of any synthesized Gemini surfactant at any tested temperature higher than the change in free energy of micellization ΔG^o_{mic}. From that, we conclude that the synthesized Gemini surfactants tend firstly to adsorb at the air–water interface until maximum surface saturation then the monomers aggregates in bulk in clusters forms. The change in the entropy of both micellization ΔS_{mic} and adsorption ΔS_{ads} values was listed in Table 2, and it found to be positive values indicating the disruption of water structure around the tail of Gemini surfactant when they transfer from the aqueous

Table 2
Micellization and adsorption thermodynamic parameters of the prepared Gemini 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}
C8-S3-C8	25	−38.52	–	–	−48.13	–	–
	40	−42.14	33.49	0.241	−52.60	40.78	0.298
	60	−45.10	4.21	0.148	−56.43	7.35	0.191
C12-S3-C12	25	−46.91	–	–	−57.06	–	–
	40	−52.42	62.62	0.367	−63.43	69.53	0.425
	60	−56.39	9.83	0.199	−68.63	17.98	0.260
C16-S3-C16	25	−54.27	–	–	−62.27	–	–
	40	−61.98	98.89	0.514	−71.12	113.59	0.590
	60	−66.71	12.18	0.237	−77.19	24.03	0.304

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)
		C8-S3-C8	C12-S3-C12	C16-S3-C16		
Bacillus subtilis	G^+	15	16	13	Ampicillin	20
Escherichia coli	G^-	16	18	14	Ampicillin	22
Pseudomonas aeruginosa	G^-	16	17	13	Ampicillin	17
Staphylococcus aureus	G^+	17	17	14	Ampicillin	18
Aspergillus flavus	Fungus	0.0	15	12	Amphotericin B	17
Candida albicans	Fungus	15	14	12	Amphotericin B	19

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 greater freedom of hydrophobic part through motion to the interface than to form micelle [41–43].

3.7. Antimicrobial activity of synthesized Gemini surfactants

The antibiotic effect of synthesized Gemini surfactants against some Gram positive and negative bacteria and fungi has been recorded in Table 3, showing very good activity compared to the reference used. By analyzing the data in Table 3, it was found that the antibiotic activity of synthesized Gemini surfactants is hydrophobic chain dependant; where the activity was found to increase by lengthening the tail until Gemini surfactants with tail of twelve carbon atoms (C12-S3-C12) then it decrease with synthesized surfactants of sixteen carbon atom (C16-S3-C16); this trend known by cut-off effect. [44–46].

There are some parameters, which are responsible for that phenomenon like critical micelle concentration (CMC) of the used Synthesized Gemini surfactant, the change in the free energy of adsorption ΔG^o_{ads} on the bacteria cell membrane, the size of diffused Gemini monomers and their micelle and the hydrophobicity of surfactant. Increasing the chain length of the two tailed of Gemini surfactants accompanied by decreasing in the CMC as previously discussed, hence the concentration at surface becomes lower, consequently the activity of C8-S3-C8 > C12-S3-C12 > C16-S3-C16. Increasing the hydrophobic character, the adsorption rate at the membrane interface is higher as discussed previously, so it predicted that C16-S3-C16 > C12-S3-C12 > C8-S3-C8. Other theories ascribed 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 synthesized Gemini surfactants with two tails of twelve-carbon atom have the maximum antibiotic effect [47–50]. Fig. 9 shows the main composition of Gram-positive and Gram-negative bacteria membrane. The expected mechanism of synthesized Gemini surfactant as 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 [51–53].

4. Conclusion

A new series from amido-amine Gemini cationic surfactants were prepared and their chemical structures were confirmed using Fourier transform infrared spectroscopy and proton nuclear magnetic resonance. The determined critical micelle concentrations from surface tension and conductive measurements were similar. The critical micelle concentration obtained from conductive measurements are slightly higher than that obtained from surface tension measurements due to premicellar region The determined surface parameters from surface tension are hydrophobic and temperature dependent. The critical micelle concentration of the synthesized amido-cationic surfactants decreases by increasing the hydrophobic chain length and the solution

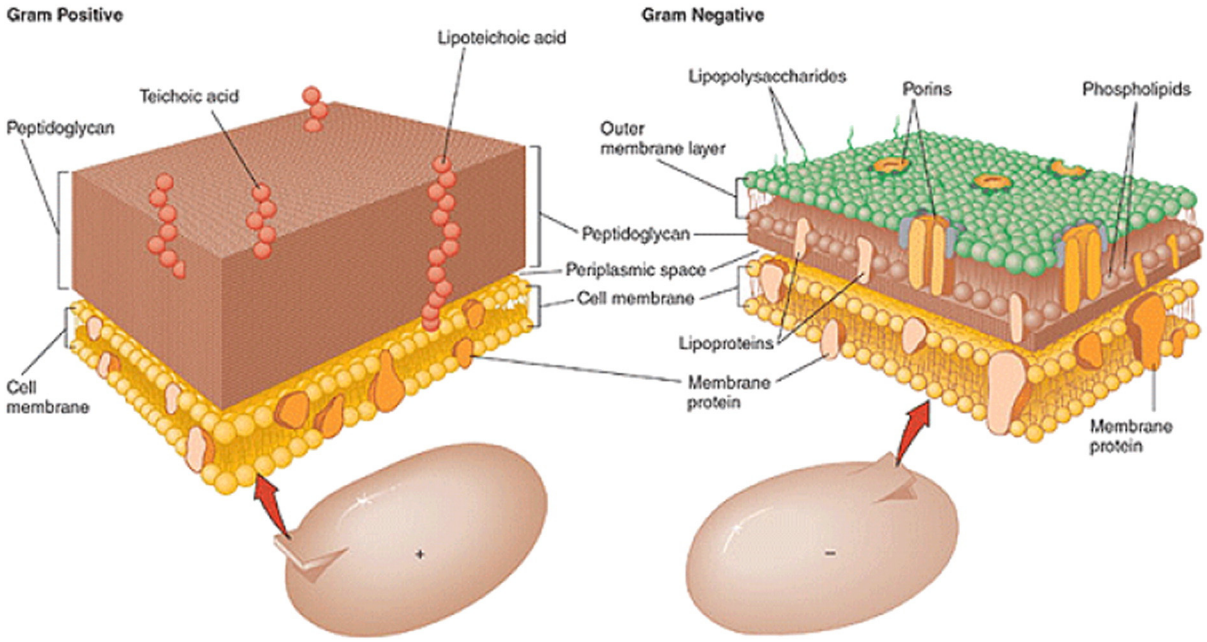

Fig. 9. The bacterial cell walls structure.

temperature. By increasing the length of hydrophobic chain and temperature, the adsorption at air/water interface and micellization in solution bulk increase. The conductivity of synthesized Gemini surfactant solution increases by elevating the temperature and decrease by increasing the hydrophobic chin length. The adsorption process is more favorable than micellization by increasing the hydrophobicity and solution temperature. The synthesized cationic surfactant showed good antibiotic effect against bacteria and the synthesized C12-S3-C12 surfactant has the maximum activity.

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References

[1] I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.M.Y. El-Awady, S.S.M. Shaban, J. Ind. Eng. Chem. 20 (2014) 3430–3439.
[2] M. Priyanka, S.M. Phadnis, R.R. Bhonde, B.L.V. Prasad, Colloids Surf. B: Biointerfaces 73 (2009) 224–228.
[3] T. Mishraa, R.K. Sahu, S.-H. Lim, L.G. Salamanca-Riba, S. Bhattacharjee, Mater. Chem. Phys. 123 (2010) 540–545.
[4] A.J. Kora, R. Manjusha, J. Arunachalam, Mater. Sci. Eng. C 29 (2009) 2104–2109.
[5] M. EL-Sukkary, A. Deeb, I. Aiad, M.Y. El-Awady, H. Hamed, S.M. Shaban, Pet. Sci. Technol. 28 (2010) 1158–1169.
[6] N.A. Negm, S.M. Tawfik, M.I. Abdou, E.A. Badr, F.M. Ghuiba, J. Surfactant Deterg. 18 (2015) 309–319.
[7] A.A. Olajire, Energy 77 (2014) 963–982.
[8] S.M. Shaban, I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.M.Y. El-Awady, J. Mol. Liq. 203 (2015) 20–28.
[9] A. Marcomini, F. Filipuzzi, W. Giger, Chemosphere 17 (5) (1988) 853–863.
[10] M. Sadeghi-Kiakhani, A.R. Tehrani-Bagha, Colloids Surf. A Physicochem. Eng. Asp. 479 (2015) 52–59.
[11] B. Li, Q. Zhang, Y. Xia, Z. Gao, Colloids Surf. A Physicochem. Eng. Asp. 470 (2015) 211–217.
[12] C. Oliviero, L. Coppola, C. La Mesa, G.A. Ranieri, M. Terenzi, Colloids Surf. A Physicochem. Eng. Asp. 201 (2002) 247–260.
[13] S. Yang, M. Gao, Z. Luo, Q. Yang, Chem. Eng. J. 268 (2015) 125–134.
[14] P.A.R. Pires, O.A. El Seoud, J. Colloid Interface Sci. 304 (2006) 474–485.
[15] Y. Jiang, T. Geng, Q. Li, G. Li, H. Ju, J. Mol. Liq. 204 (2015) 126–131.
[16] B. Kumar, D. Tikariha, K.K. Ghosh, P. Quagliotto, J. Mol. Liq. 172 (2012) 81–87.
[17] C. Perez, A. Pauli, P. Bazerque, Acta Biol. Med. Exp. 15 (1990) 113–115.
[18] S.M. Shaban, I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.Y. El-Awady, J. Mol. Liq. 207 (2015) 256–265.
[19] M.J. Monteiro, F.F. Camilo, M.C.C. Ribeiro, R.M. Torresi, J. Phys. Chem. B 114 (2010) 12488.
[20] K. Tsunashima, Y. Ono, M. Sugiya, Electrochim. Acta 56 (2011) 4351.
[21] B. Gao, M.M. Sharma, J. Colloid Interface Sci. 404 (2013) 80–84.
[22] X. Zhong, J. Guo, L. Feng, X. Xu, D. Zhu, Colloids Surf. A Physicochem. Eng. Asp. 441 (2014) 572–580.
[23] L. Zhi, Q. Li, Y. Li, Y. Song, Colloids Surf. A Physicochem. Eng. Asp. 436 (2013) 684–692.
[24] Kabir-ud-Din, M.A. Rub, A.Z. Naqvi, Colloids Surf. B 82 (2011) 87–94.
[25] R. Kamboj, S. Singh, V. Chauhan, Colloids Surf. A Physicochem. Eng. Asp. 441 (2014) 233–241.
[26] S.M. Shaban, I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.Y. El-Awady, J. Ind. Eng. Chem. 20 (2014) 4194–4201.
[27] P. Patial, A. Shaheen, I. Ahmad, J. Surfactant Deterg. 17 (2014) 929–935.
[28] S. Chauhan, M. Kaur, K. Kumar, M.S. Chauhan, J. Chem. Thermodyn. 78 (2014) 175–181.
[29] I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.Y. El-Awady, S.M. Shaban, J. Ind. Eng. Chem. 20 (2014) 1633–1640.
[30] S. Chauhan, K. Sharma, J. Chem. Thermodyn. 71 (2014) 205–211.
[31] V. Chauhan, S. Singh, R. Mishra, G. Kaur, J. Colloid Interface Sci. 436 (2014) 122–131.
[32] I. Ahmad, P. Patial, C. Kaur, S. Kaur, J. Surfactant Deterg. 17 (2014) 269–277.
[33] C. Ren, F. Wang, Z. Zhang, H. Nie, N. Li, M. Cui, Colloids Surf. A Physicochem. Eng. Asp. 467 (2015) 1–8.
[34] X.F. Geng, X.Q. Hua, J.J. Xia, X.C. Jia, Appl. Surf. Sci. 271 (2013) 284–290.
[35] P. Patial, A. Shaheen, I. Ahmad, J. Ind. Eng. Chem. 20 (2014) 4267–4275.
[36] W. Qiao, J. Li, H. Peng, Y. Zhu, H. Cai, Colloids Surf. A Physicochem. Eng. Asp. 384 (2011) 612–617.
[37] D.-Y. Zhu, F. Cheng, C. Yu, S.-C. Jiang, Colloids Surf. A Physicochem. Eng. Asp. 397 (2012) 1–7.
[38] R. Sharma, S. Mahajan, R.K. Mahajan, Colloids Surf. A Physicochem. Eng. Asp. 427 (2013) 62–75.
[39] K. Sharma, S. Chauhan, Colloids Surf. A Physicochem. Eng. Asp. 453 (2014) 78–85.
[40] R. Zana, Langmuir 12 (1996) 1208–1211.
[41] D. Tikariha, N. Singh, M.L. Satnami, K.K. Ghosh, N. Barbero, P. Quagliotto, Colloids Surf. A Physicochem. Eng. Asp. 411 (2012) 1–11.
[42] L.-H. Lin, Y.-W. Ye, K.-M. Chen, Colloids Surf. A Physicochem. Eng. Asp. 416 (2013) 1–8.
[43] M.S. Ali, M. Suhail, G. Ghosh, M. Kamil, Kabir-ud-Din, Colloids Surf. A Physicochem. Eng. Asp. 350 (2009) 51–56.
[44] J. Haldar, P. Kondaiah, S. Bhattacharya, J. Med. Chem. 48 (2005) 3823–3831.
[45] S.M. Shaban, I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.Y. El-Awady, J. Ind. Eng. Chem. 20 (2014) 4473–4481.
[46] H.M. Willemen, L.C.P.M. de Smet, A. Koudijs, M.C.A. Stuart, I.G.A.M. Heikamp-de Jong, A.T.M. Marcelis, E.J.R. Subholter, Angew. Chem. Int. Ed. 41 (2002) 4275–4277.
[47] L. Perez, M.T. Garc'ıa, I. Ribosa, P. Vinardell, A. Manresa, M.R. Infante, Environ. Toxicol. Chem. 21 (2002) 1279–1285.
[48] M.R. Infante, L. P'erez, A. Pinazo, in: K. Holmberg, M. Dekker (Eds.),Novel Cationic Surfactants from Arginine, Novel Surfactants, Preparation, Applications and Biodegradability, Surfactant Science Series, 2003.
[49] M. Pringle, K. Brown, K. Miller, Mol. Pharmacol. 19 (1981) 49–55.
[50] I. Chernomordik, M.M. Kozlov, J. Zimmerberg, J. Membr. Biol. 146 (1995) 1–14.
[51] J.W. Costerton, K.-J. Cheng, J. Antimicrob. Chemother. 1 (1975) 363–377.
[52] L. Tavano, M.R. Infante, M. Abo Riya, A. Pinazo, M.P. Vinardell, M. Mitjans, M.A. Manresa, L. Perez, Soft Matter 9 (2013) 306–319.
[53] I. Aiad, M.M. EL-Sukkary, A. El-Deeb, M.Y. El-Awady, S.M. Shaban, J. Surfactant Deterg. 15 (2012) 359–366.