

Surface and Biological Activity of Some Novel Cationic Surfactants

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ABSTRACT

In this article we take steps toward the development of bactericidal and fungicidal synthetic cationic surfactants by reaction of decyl, dodecyl or tetradecyl amine with acetic acids or hydrochloric to produce a series of quaternary ammonium salts which consequently converted to copper and cobalt cationic complexes via complexing the first series compounds with copper (II) or cobalt (II) ions. Surface properties of these surfactants were investigated. The surface properties studies included critical micelle concentration (CMC), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}). Free energy of micellization (ΔG_{mic}°) and adsorption (ΔG_{ads}°) were calculated. The antimicrobial activity was determined via the inhibition zone diameter of the prepared compounds which measured against five strains of representative group of microorganisms. FTIR spectra, elemental analysis and H^1 NMR spectrum were performed to insure the purity of the prepared compounds.

Key words: Critical micelle concentration, cationic surfactant, biocidal activity

INTRODUCTION

Cationic surfactants have been the focus of wide spread interest over decades due to their ability to self-assemble in super molecular structures such as micelles⁽¹⁾. The aggregates formed create sharp polarity gradients at the interface and define clear hydrophobic regions in an aqueous solution⁽²⁾. Those properties are of fundamental importance for the creation of new materials⁽³⁾.

Surfactant metal complexes are expected to provide a wide range of interesting phenomena on the aggregation behavior in aqueous solution due to a variety of their charge numbers, size and extent of hydrophobicity by a combination of a central metal and ligands⁽⁴⁾. However, their physical properties in solutions have not been extensively studied⁽⁵⁻⁹⁾. In the studies so far performed, novel characters of surfactant metal complexes have been revealed, and the results should provide significant information on surfactant solution chemistry. Metalloaggregates are made of surfactants that combine a metal-coordinating polar head to hydrophobic tail⁽¹⁰⁻¹²⁾. The polar head of the surfactant is functionalized with metal ions are bound to and surrounded by hydrophobic region, similar to the situation found in metalloproteinase⁽¹³⁾. The antimicrobial action of cationic surfactant is based on their ability to disrupt the integral bacterial membrane by a combined hydrophobic and electrostatic adsorption phenomenon at the membrane water interface making disorganization⁽¹⁴⁾. The pathogenic bacterial cell membrane is predominantly negatively charged as compared with eukaryotic cells⁽¹⁵⁾. Hence the positive charge of the cationic amphiphile facilitates their interactions with bacterial membrane. In this work, two series of cationic surfactants were prepared in the laboratory; one of them is metal-complex type. The surface and biocidal activity were determined for both types and then comparison was made between the normal cationic surfactants and metal complex ones.

EXPERIMENTAL PROCEDURE

Materials:

The entire chemical used throughout this investigation is supplied from international companies. All of them were in analytical grade as shown in Table 1.

Table 1: Chemical used throughout the investigation

Materials	Molecular weight	Source
Acetic acid	60.5	Hungary Co
Hydrochloric acid	36.5	Aldrich
Decylamine	157.3	Merck
Dodecylamine	185.4	Merck
Tetradecylamine	199.4	Merck
Cobalt acetate	249.08	Aldrich
Copper acetate	199.65	Aldrich
Cobalt chloride	237.93	Aldrich
Copper chloride	170.4	Aldrich

Synthetic Procedure

Synthesis of decyl, dodecyl and tetradecyl amine acetates

Stoichiometric amounts of acetic acid were mixed with decyl, dodecyl or tetradecyl amine at room temperature then shaking well. A clouding of the solution occurred, followed by white precipitate, which increased rapidly in quantity as the reaction progressed. The precipitant was filtered, and then recrystallized by petroleum ether (60°). The products are designated as I_a, II_a and III_a and have the general formula:

$RN^+H_3 COOCH_3$ where R = decyl, dodecyl and tetradecyl, respectively.

Synthesis of decyl, dodecyl and tetradecyl amine chlorides

They are best prepared by the neutralization of decyl, dodecyl or tetradecyl amine with hydrochloric acid and then stirring until the precipitation is stopped. The precipitant was filtered, and then recrystallized by ethyl alcohol. The products are designated as I_d, II_d and III_d and have the general formula:

$RN^+H_3 Cl$ where R = decyl, dodecyl and tetradecyl, respectively.

Synthesis of metal complexes

Copper and cobalt acetate complexes were prepared by refluxing two moles of cationic acetates (I_a, II_a and III_a) with one mole of copper or cobalt acetate in ethyl alcohol for two hours. The products are designated as (I_{b,c}, II_{b,c} and III_{b,c}), whereas (I_{e,f}, II_{e,f} and III_{e,f}) copper or cobalt chloride complexes were prepared by refluxing two moles of cationic chlorides (I_d, II_d and III_d) with one mole of copper or cobalt chloride in ethanol for two hours, the products purified and recrystallized three times in petroleum ether and then washed with diethyl ether. The products kept in desiccators up to use it. General formula for the metal complexes

$[RN^+H_3]_2 [M (CH_3COO)_4]^{-2}$ & $[RN^+H_3]_2 [M (Cl)_4]^{-2}$
Where R = decyl, dodecyl and tetradecyl, respectively, M: Co⁺² or Cu⁺²

Table 2: Identification of the prepared acetate cationic surfactant and their metal complexes I_{a-c}-III_{a-c}

Compound no.	Chemical formula	Name
I _a	C ₁₂ H ₂₇ N O ₂	Decyl amine acetate
I _b	C ₂₈ H ₆₀ N ₂ O ₈ Co	Decyl amine tetra acetato cobaltate complex
I _c	C ₂₈ H ₆₀ N ₂ O ₈ Cu	Decyl amine tetra acetato copperate complex
II _a	C ₁₄ H ₃₁ N O ₂	Dodecyl amine acetate
II _b	C ₃₂ H ₆₈ N ₂ O ₈ Co	Dodecyl amine tetra acetato cobaltate complex
II _c	C ₃₂ H ₆₈ N ₂ O ₈ Cu	Dodecyl amine tetra acetato copperate complex
III _a	C ₁₆ H ₃₅ N O ₂	Tetradecyl amine acetate
III _b	C ₃₆ H ₇₆ N ₂ O ₈ Co	Tetradecyl amine tetra acetato cobaltate complex
III _c	C ₃₆ H ₇₆ N ₂ O ₈ Cu	Tetradecyl amine tetra acetato copperate complex

Table 3: Identification of the prepared chloride cationic surfactant and their metal complexes I_{d-f}-III_{d-f}

Compound no.	Chemical formula	Name
I _d	C ₁₀ H ₂₄ N Cl	Decyl amine chloride
I _e	C ₂₀ H ₄₈ N ₂ Cl ₄ Co	Decyl amine tetra chloride cobaltate complex
I _f	C ₂₀ H ₄₈ N ₂ Cl ₄ Cu	Decyl amine tetra chloride copperate complex
II _d	C ₁₂ H ₂₈ N Cl	Dodecyl amine chloride
II _e	C ₂₄ H ₅₆ N ₂ Cl ₄ Co	Dodecyl amine tetra chloride cobaltate complex
II _f	C ₂₄ H ₅₆ N ₂ Cl ₄ Cu	Dodecyl amine tetra chloride copperate complex
III _d	C ₁₄ H ₃₂ N Cl	Tetradecyl amine chloride
III _e	C ₂₈ H ₆₄ N ₂ Cl ₄ Co	Tetradecyl amine tetra chloride cobaltate complex
III _f	C ₂₈ H ₆₄ N ₂ Cl ₄ Cu	Tetradecyl amine tetra chloride copperate complex

Methods of Analysis and Instruments

Infrared spectra for prepared surfactants were measured using Avatar 230 FTIR spectrophotometer to measure intensity of absorption bands for the prepared surfactants. The measurements were carried out in Egyptian Petroleum Research Institute.

The elemental analysis for the obtained surfactants was carried out using Elemental Analyzer Model Varioelemenrar. The measurements were carried out in in micro Analytical Center, Faculty of Science, Cairo University.

Proton Nuclear Magnetic Resonance Measurements (¹H NMR) were performed on a Varian-Gemini-200 instrument and the samples were run in deuterated chloroform (CDCl₃, Cambridge Isotope Laboratories) in micro Analytical Center, Faculty of Science, Cairo University.

Atomic Absorption Spectrometer (AAS) measurements for copper and cobalt analyses were performed with AAS (Flame absorption) PerkinElmer; the detection limits for these analyses are 0.005 g/20 ml for cu, 0.003 g/20 ml for cobalt, in micro Analytical Center, Faculty of Science, Cairo University.

Evaluation Method of Surface active Properties

Surface and interfacial tension measurements

Surface and interfacial tension measurements of the prepared surfactants were made at room temperature (25°C) with Du Nouy tensiometer (Kruss type 8451) using distilled water solution of 0.1% weight concentration⁽¹⁶⁾.

The surface tension of the used distilled water was 73 mN/m and the interfacial tension between medicinal paraffin oil and distilled water was 56.2 mN/m. Surfactant solutions were aged for 1/2h before any measurements were made. Three readings were made on each sample to determine any change with time and to obtain an average value⁽¹⁷⁾.

Emulsifying power

Emulsifying power or emulsifying time (in sec) was determined according to the method described in^(18, 19)

In a measuring cylinder, surfactant solution (0.1 g/10 ml) and paraffin oil (10 ml) were mixed. After vigorous shaking (10 times) ,

The tube was allowed to stand till any separation of the two phases appeared.

Efficiency (PC₂₀)

The efficiency (PC₂₀) was determined by the concentration (mol/dm³) capable to suppress the surface tension by 20 dyne/cm⁽²⁰⁾. The efficiency have been determined by extrapolating from $\gamma = 52$ to the linear portion before CMC of the γ versus-Log C plot⁽¹⁴⁾, at 25°C.

Effectiveness (Π_{cmc}):

The surface tension " γ_{cmc} " values at CMC were used to calculate values of surface pressure (effectiveness) form the following equation:

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc}$$

Where γ_0 is the surface tension measured for the pure water at the appropriate temperature and γ_{cmc} is the surface tension at CMC. The effectiveness of adsorption is an important factor to determine such properties of surfactant as foaming, wetting and emulsification, since tightly packed coherent interfacial films have very different interfacial properties than loosely packed, non coherent films⁽²¹⁾.

Determination of Critical Micelle concentration

CMC of the prepared surfactant was determined by the surface tension method⁽²²⁾. In this methods values of the surface tension obtained for various concentrations of aqueous solutions of the prepared surfactants were plotted vs. the corresponding concentrations

Maximum surface excess Γ_{max}

The surface excess concentration is the surface concentration at surface saturation; the maximum surface excess Γ_{max} is a useful measure of the effectiveness of adsorption of the surfactant at the water-air interface, since it is the maximum value to which adsorption can attain.

$$\Gamma_{Max} = \frac{1}{2.303 RT} \left(\frac{\delta \gamma}{\delta \log c} \right)_T$$

Where $R = 8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$, T is absolute temperature, $(\delta \gamma / \delta \log C)$ is the slope of the. γ Vs. Log c plot at room temperature⁽²³⁾.

A substance which lowers the surface tension is thus present excess at or near the surface, i.e. when the surface tension decreases with increasing the activity of the surfactant, Γ is positive.

Minimum surface Area (A_{min}) A_{min} is the minimum area per molecule of the prepared Compounds at the interface and was calculated from the following equation :

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

Where N is Avogadro's number and Γ_{max} is the maximum surface excess.

The standard free energies of micellization ΔG_{mic}° and adsorption ΔG_{ads}° Understanding the process of micellization and adsorption are important for explanation of the effects of structural and environmental factors on the value of the CMC and for predicting the effects on it of new structural and environmental variations. Standard free energy of micellization ΔG_{mic}° , and adsorption ΔG_{ads}° , have played an important role in such understanding. The standard free energy of micellization and adsorption are given by:

$$\Delta G_{mic}^{\circ} = RT \ln CMC$$

$$\Delta G_{ads}^{\circ} = \Delta G_{mic}^{\circ} - 6.023 \times 10^{-1} \Pi_{CMC} A_{min}$$

The interfacial activity ($I_{activ.}$).

It is expressed by physicochemical parameter $\Delta G_{ads} / A_{min}$, where ΔG_{ads} is the standard free energy of adsorption of the surfactant at the air /solution interface and A_{min} is the minimum cross sectional area of the surfactant.

Measurement of antimicrobial activity using diffusion disc method:

A filter paper sterilized disc saturated with measured quantity of the sample is placed on plate containing solid bacterial medium (nutrient agar broth) or fungal medium (Dox's medium) which has been heavily seeded with the spore suspension of the tested organism. After incubation, the diameter of the clear zone of inhibition surrounding the sample is taken as a measure of inhibitory power of the sample against the particular test Organism (24-27).

RESULTS AND DISCUSSION

The prepared surfactants were confirmed by different means. FTIR series spectrometer Table (4), elemental analysis Table (5, 6), H^1NMR spectroscopy and AAS for copper and cobalt complexes the results were found to be compatible with the supposed structure.

Results of FTIR data

The chemical structures for surfactant samples were accorded FT-IR Table (4). The FT-IR absorption spectra showed, generally absorption band around 2639.97-2679.36 cm^{-1} region indicating the primary amine band was disappeared and the presence of ammonium ion (RN^+H_3) in addition to strong band at 724.87 cm^{-1} indicating for the presence of multiple (CH_2) group. The very strong band at (2848-2852.13) cm^{-1} region for all the prepared compounds due mainly to the methyl symmetric stretching vibration. The very strong band at (2958-2965) cm^{-1} for all prepared compounds due mainly to the methylene as symmetric stretching vibration.

The assignment is generally in agreement with the expected correlation.

Table (4): characteristic peaks of the prepared compounds

Function group		Wave no. (cm^{-1})			
		I _a	I _c	III _d	III _r
CH ₂	Multiple (CH ₂) rock	724.87	719.23	720.86	718.35
	Asymmetric bending	1467.42	1466.49	1463.86	1466.43
	Asymmetric stretch	2958.04	2962.89	2963.78	2965
CH ₃	Symmetric bending	1994.29	1403.8	1396.94	1400.56
	Symmetric stretch	2848	2849.22	2850.72	2852.13
Ammonium ion (RN^+H_3)		2639.97	2603.4	2679.36	2665.37

The first peak, methyl protons (H_a) have two neighboring protons, these protons, appear as three line signal (triplet) at $\delta = 0.84$ ppm. The second peak, methylene protons (H_b) have five neighboring protons which appear as six line signal (sextet) at 1.5 ppm. The third peak, methylene protons (H_c)_n have four neighboring protons which appear as five line signal (quintet) at $\delta=1.23$ ppm. The fourth peak, methylene protons have four neighboring which appear as five line signal (quintet), this signal is shifted to up field because of the electro negativity of nitrogen atom and therefore appear at $\delta=2.5-2.7$ ppm. The fifth peak, methylene protons (H_e) have five neighboring protons, which appear as six line signal (sextet) at $\delta=4.364$ ppm. The sixth peak, amine protons (H_f) have five neighboring protons which appear as six line signal (sextet) at $\delta=7$ ppm . It is shifted to up field due to positive charge on nitrogen atom.

Results of Atomic Absorption spectrometer

AAS results indicate that the theoretical and the found values are very close.

Surface properties

Surface properties of the prepared cationic surfactants were measured and tabulated in Table (7, 8).

Surface and interfacial tensions

Surface and interfacial tensions of the prepared cationic surfactants and their corresponded metal complexes were measured at 25°C as shown in Table (7, 8). In case of the parent cationics ($I_{a,d}$ - $III_{a,d}$) the surface and interfacial tensions value of their solutions decreases by increasing methylene units .That behavior is due to the increasing hydrophobic chain length leads to decreasing the aqueous solubility and migrate the surfactant from the bulk to the interface ⁽²⁸⁾,The surface tension values of the cationic complexes ($I_{b,c}$ - $III_{b,c}$), ($I_{e,f}$ - $III_{e,f}$) were found in lower values than their parent cationic surfactants. That could be referred to the increasing in the hydrophobicity of these complexes than the parent cationics, which is due to the presence of two ligands coordinated to the metal ion within their that giant structure of the complex contain higher number of methylene group, i.e more non polar chains. Then the water/surfactant molecules interactions increased, which forced them to the air water interface ⁽²⁹⁾. Hence, the surface tension depressed considerably, Table (7, 8). In fact these results suggest that, two alkyl chains in one molecule linked by a metal ion enhance the adsorption and aggregation properties, by strengthening the inter-or intermolecular hydrophobic interaction ⁽³⁰⁾. The uniqueness of the metal- surfactant coordination complexes lies in the fact that the bond between the head group and the tail part of the surfactant is a coordinate bond and the surfactant contains a higher charge on the head group which leads to more repulsion in the bulk of aqueous solution and increasing adsorption onto surface.

Emulsifying power

It's clear from Table (7, 8) that all the prepared surfactants show adequate emulsifying power towards paraffin oil.

CMC of the prepared surfactants

The results in Table (9, 10) and fig. (1-6) on complexing the cationic surfactants with cobalt or copper ions, high depression was observed in CMC values compared with those of the parent cationics. That fact could be explained from the unique property of the metal complexes in water. That is the complexes retain its unity in their solutions, which increased their volume in the aqueous media and then repulsion is occurred between the hydrophobic chain and water molecules. That repulsion facilitates two processes in the same time.

1-Adsorption of the molecules (metal complex) at the air/water interface at extremely lower concentrations (below CMC).

2-Micellization of molecules (metal complex) at concentration lower than their parent cationics.

The application of these molecules in commercial processes could allow us to dramatically reduce the concentration of surface active material used for the same level of performance. Thus, it is concluded that these metal surfactant complexes have more capacity to associate themselves, forming aggregates, compared to those of ordinary synthetic quaternary ammonium salts. This suggests that the introduction of a metal ion to the hydrophilic part of the amphiphile can remarkably enhance the ability of aggregation.

Effectiveness " Π_{cmc} "

The most efficient one is that gives the greatest lowering in surface tension for a critical micelle concentration (CMC). (Π_I , Π_{II}) were found to be the most efficient once Table (9, 10) because they achieved the maximum reduction of the surface tension at CMC fig. (5, 6).

Efficiency " P_{C20} "

Values of efficiency of the prepared surfactants are shown in Table (9, 10), the efficiency increase with increasing molar ratio of methylene units. These due to the fact that the efficiency of adsorption at interfaces increase linearly with increase in the carbon atoms in hydrophobic group. ⁽²¹⁾

Maximum surface excess Γ_{max}

It is evident from Table (9, 10) that in case of prepared parent cationic surfactants by increasing the number methylene units Γ_{max} increases. Complexing the cationic surfactant with cobalt and copper ions contributes to migration of molecules to the water-air interface causing a consequent high increase in Γ_{max} values.

Minimum area per molecule A_{min}

Results given in Table (9, 10) indicate that by consequence increase of Γ_{max} leads to crowding occurred at the interface which causing decreasing in A_{min} values.

The standard free energies of micellization ΔG°_{mic} and adsorption ΔG°_{ads} .

From Table (9,10) values of ΔG°_{mic} and ΔG°_{ads} are always negative indicating the spontaneously of these two processes but there is more increase in negativity of ΔG°_{ads} rather than those of micellization indicating the tendency of the molecules to be adsorbed at the interface.

Antimicrobial activity of the prepared cationic surfactants The cell membrane of microorganisms is composed of several lipids and protein layers arranged together in a specific arrangement called the bilayer (or multilayer lipoprotein structure). The presence of the lipids as a building unit in the cell membrane acquires them their hydrophobic character ⁽³¹⁾. The selective permeability of the lipoprotein membrane represents the main function, which control the biological reaction in the cell. Hence, any factor influences that permeability causes a great damage to the microorganisms, which leads it to die. The cationic surfactants have a unique ability of adsorption at the interfaces where the pathogenic bacterial cell membrane is predominantly negatively charged as compared with eukaryotic cells ⁽¹⁵⁾. Hence the positive charge of the cationic amphiphile facilitates their interaction with the bacterial membrane, which acquires them a good Biocidal activity towards microorganisms ⁽³²⁻³³⁾. The adsorption at the water/cell membrane increases the hydrophobicity of that membrane which, increase its permeability towards the media ingredients ⁽³⁴⁾. That resulting in disturbing the biological reactions occurred within the cell cytoplasm. The optimal activity towards a variety of bacterial species for many water soluble cationic surfactants appears to occur at C_{10} - C_{14} carbon atoms. ⁽³⁵⁻³⁹⁾ In this study the prepared quaternary ammonium salts containing hydrophobic chains of varying length were tested against pathogenic gram-positive (*Staphylococcus aureus*, *Streptococcus faecalis*, *Bacillus subtilis*) and gram-negative (*Escherichia coli*) bacteria and

also, some pathogenic fungi (*Candida albicans*). The results of antimicrobial activity of the synthesized surfactants against pathogenic bacteria and fungi recorded in Table (11, 12). Table (11, 12) indicates that the synthesized QAS have antimicrobial activity. the difference in activity depends on the length of hydrophobic chains and the interfacial properties of the prepared surfactants. The relationship between interfacial properties of the surfactants and their biological activity for some strains of microorganisms was studied by Stephen W.M. and Donald J.V. ⁽⁴⁰⁾, in each case the interfacial activity is expressed by the physicochemical parameter $\Delta G_{ads} / A_{min}$. Table (11, 12) and Fig. (7-12) indicates that all the synthesized QAS have antimicrobial activity which expressed by inhibition zone diameter. The difference in activity depends on the length of hydrophobic chains and the interfacial properties of the prepared surfactants. As shown in fig. (7-12) there is an excellent linear relation ship between interfacial activity and biological activity in case of metal complex surfactants, the biological activity was increased to higher extent .That increase could be explained through their ability towards adsorption at the cell of the tested microorganisms which appear as increase in physicochemical parameter $\Delta G_{ads} / A_{min}$ due to their high hydrophobicity, which acquired from the great number of methylene units within complex molecules .In comparing the biological activity between copper and cobalt complexes, copper complexes showed higher biological activity .The difference was noted in small cases and for small extend. The increase in the activity for copper complexes is attributed to the lower electro negativity and large volume of the copper ions which increased their molecular area. Hence, the effective area of the complex molecules on the cell membrane will increase resulting on the higher biological action. ⁽⁴¹⁾

CONCLUSION

1. The synthesized cationic surfactants showed antimicrobial activity towards gram-positive and gram negative bacteria and fungi.
2. Complexing of cationic surfactants with cobalt and /or copper ion increased their interfacial and antimicrobial activity externally.
3. The optimal length of the alkyl chain has been noted to be twelve carbon atoms for antimicrobial activity.

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Table 7: Surface properties of acetate surfactants

Surfactants	Surface tension (mN/m)	Interfacial tension (mN/m)	Emulsifying power (min)
I _a	39	14	67
I _b	38	14	67
I _c	37.5	12	69
II _a	35	10.4	95
II _b	34	10.6	85
II _c	34	12	100
III _a	36	15	134
III _b	34	14	140
III _c	34	13	136

Table 8: Surface properties of chloride surfactants

Surfactants	Surface tension (mN/m)	Interfacial tension (mN/m)	Emulsifying power (min)
I _d	39	8	94
I _e	38	7	90
I _f	38	8	95
II _d	37	6	112
II _e	36	8	114
II _f	35	8	117
III _d	35	10	189
III _e	34	9	185
III _f	33	8	184

Table 9: The critical micelle concentration (CMC) and surface parameters of the cationic acetate surfactants at 25 °C

surfactant	CMC $\times 10^{-3}$	γ_{CMC} (mN/m)	Π_{CMC} (mN/m)	P_{C20} (Mole/L)	$\Gamma_{max} \times 10^{-11}$ (Mole/cm ²)	A_{min} (nm ²)	ΔG_{ads}	ΔG_{mic}	$\Delta G_{ads} / A_{min}$
I _a	2.4	38	34	3.7	8.3883	1.967	-70.14	-29.86	-35.66
I _b	1.1	37	35	4.0	9.55178	1.727	-70.14	-33.73	-40.61
I _c	1.09	35	37	4.1	9.55179	1.7271	-72.26	-33.77	-41.84
II _a	2.3	35.5	36.5	4.02	9.17623	1.798	-69.59	-30.07	-38.71
II _b	0.9	34	38	4.01	10.3388	1.596	-75.9	-39.41	-47.56
II _c	0.9	31	41	4.292	10.4766	1.574	-78.27	-39.42	-49.73
III _a	2.7	37	35	4.0	10.41204	1.63	-64.43	-30.07	-39.53
III _b	1.3	34	38	4.299	10.459	1.577	-68.99	-32.89	-43.74
III _c	1.2	33	39	4.4	10.6547	1.548	-69.65	-33.29	-44.99

Table 10: The critical micelle concentration (CMC) and surface parameters of the cationic chloride surfactants at 25 °C

surfactant	CMC $\times 10^{-3}$	γ_{CMC} (mN/m)	Π_{CMC} (mN/m)	P_{C20} (Mole/L)	$\Gamma_{max} \times 10^{-11}$ (Mole/cm ²)	A_{min} (nm ²)	ΔG_{ads}	ΔG_{mic}	$\Delta G_{ads} / A_{min}$
I	2.5	33	39	3.05	8.20	2.013	-76.939	-29.65	-38.22
J	1.4	32	40	4.006	8.56	1.927	-79.318	-32.89	-41.16
K	1.3	31	41	4.1	8.78	1.878	-79.358	-32.90	-42.25
I _d	2.6	32	40	3.65	10.91	1.513	-65.912	-29.35	-43.56
I _e	2	31	41	4.09	11.30	1.459	-66.789	-30.76	-45.7
I _f	1.7	30	42	4.25	10.92	1.511	-69.788	-31.57	-46.18
II _d	1.6	31	41	4.17	11.06	1.458	-67.86	-31.86	-46.54
II _e	1.05	30.5	41.5	4.784	11.30	1.446	-70.34	-34.19	-48.64
II _f	1	30	42	5	11.41	1.445	-70.74	-34.20	-48.96

Table (11): Antimicrobial activity of the synthesized cationic acetate surfactants against pathogenic bacteria and fungi

Sample	Inhibition zone diameter (mm/mg sample)				
	Bacillus subtilis (G ⁺)	Escherichia coli (G ⁻)	Staphylococcus aureus (G ⁺)	Streptococcus faecalis (G ⁺)	Candida albicans (fungus)
Water (control)	0.0	0.0	0.0	0.0	0.0
Tetracycline (reference)	27	31	30	34	0.0
Ia	18	17	20	19	16
Ib	20	19	22	21	18
Ic	21	20	23	22	19
IIa	28	24	25	26	25
IIb	30	26	28	29	27
IIc	31	27	29	20	29
IIIa	19	18	20	20	16
IIIb	21	20	23	23	19
IIIc	22	21	25	25	20

Table (12): Antimicrobial activity of the synthesized cationic chloride surfactants against pathogenic bacteria and fungi

Sample	Inhibition zone diameter (mm/mg sample)				
	Bacillus subtilis (G ⁺)	Escherichia coli (G ⁻)	Staphylococcus aureus (G ⁺)	Streptococcus faecalis (G ⁺)	Candida albicans (fungus)
Water (control)	0.0	0.0	0.0	0.0	0.0
Tetracycline (reference)	27	31	30	34	0.0
I _d	19	21	17	22	16
I _e	21	23	19	24	19
I _f	22	25	20	26	20
II _d	28	24	25	29	23
II _e	29	26	27	30	25
II _f	30	27	28	31	26
III _d	20	21	22	19	17
III _e	23	24	25	21	20
III _f	24	26	27	22	21











