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Preparation, Surface, and Biological Activities of Some Novel Metallosurfactants

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A series of novel metallosurfactants (III_{a-d}) was prepared and evaluated as surface active agents. The synthesis was carried out through two steps: the first was the reaction of fatty acids (I_{a-d}) (lauric, palmitic, myristic and steric acid) with morpholine (tetrahydro-1,4-oxazine) to give morpholin-4-yl-alkan-1-one (II_{a-d}), respectively. The second step is reaction of product of the first step (compounds II_{a-d}) with Fe (III) to give (III_{a-d}) metallosurfactants. The chemical structures of the prepared compounds were elucidated with elemental analysis, FTIR and ^{1}H NMR spectroscopic tools. The surface properties of the prepared metallosurfactants were determined at different temperature 25, 35, and 45°C. The surface tension (γ), critical micelle concentration (CMC), surface tension at CMC (γ_{cmc}), effectiveness (π_{cmc}), efficiency (Pc_{2o}), maximum surface excess (Γ_{max}), and minimum surface area (A_{min}) were determined. Thermodynamic data including, free energy, entropy and enthalpy changes (ΔG, ΔS, ΔH) for adsorption at the air–water interface and also for micellization in the bulk of surfactant solutions were calculated. The antimicrobial activity of the prepared compounds was determined via the inhibition zone diameter technique against Gram-positive, Gram-negative bacteria, and some fungal strains as mold and yeast. The results indicate that the prepared ferrosurfactants have a good surface properties and biological activities against the tested microorganism.

Keywords Adsorption, critical micelle concentration, metallosurfactants, micellization and antimicrobial activity

1. INTRODUCTION

The surface active agents (surfactants), literally means active at a surface. In other words, a surfactant is characterized by its tendency to absorb at surfaces and interfaces and form micelles due to their ability to self-assemble in super molecular structures among these types of surfactants is cationic one that forms like these behaviors.[1,2] The cationic surfactants are used for quite different purposes than anionic surfactants. They have a greater affinity for various surfaces form which it plays an important role in many applications as fabric softeners, adhesion promoters, corrosion inhibitors, dispersants, conditioners, germicides, and biocides. The cationic surfactants, especially those have quaternary ammonium groups have biocidal properties.[3] Metallosurfactants are surface-active molecules that integrate a metal in their structure, mostly as part of the head group.[4] Different studies were used the metal surfactants in specific proposes,[5,6] Surfactant metal complexes are expected to provide a wide range of interesting phenomena on aggregation in aqueous solution due to variations in charge numbers, size and extent of hydrophobicity through combination of the metal and ligands.[7] This upgrading to surface-active molecules can improve their employment in applications such as probes in emulsions,[8,9] optoelectronics,[10] monolayers,[11,12] and templates of mesoporous materials.[13–15] Metalloaggregates is made of surfactants that combine a metal-coordinating polar head to hydrophobic tail.[16,17] The polar head of the surfactant is functionalized with metal ions bound to and surrounded by hydrophobic region.[18] Surfactants form micelles in a solution after the critical micelle concentration (CMC), this depending on their molecular structure and environmental conditions.[19] To determine the surface properties of these surfactants and to screen their toxicity toward microorganisms, a comparative study was made between their chemical structure and their surface properties. The antimicrobial action of cationic surfactants 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.[20] The pathogenic bacterial cell membrane is predominantly negatively charged as compared with eukaryotic cells.[21] Hence, the positive charge of the cationic amphiphile facilitates their interactions with the bacterial membrane. In the present work, due to the

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metallosurfactants have various important characters, like physical activities which reduce the surface tension and biological activities where have antimicrobial activities. So, in this study a series of ferrosurfactants was prepared and their surface active properties, biological activities were studied.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1. Materials

The chemicals used throughout this work were supplied from the Morgan, Merck, Aldrich & Hi Media Company used in biological activity (see Table 1), and all solvents used were distillated before using.

2.2. Synthetic Materials

2.2.1. Synthesis of Morpholin-4-yl-Alkan-1-one (II_{a-d})

General Procedure. Mixture of (0.02 mol) of fatty acid (I_{a-d}) and (0.02 mol) of morpholine were dissolved in 50 ml of dry toluene and 0.2 wt% of P-toluene sulphonic acid were added as catalyst. The reaction mixture was heated under reflux for seven hours, the solvent was completely evaporated, and the crude products (II_{a-d}) were separated and purified with diethyl ether; the yield percentage was 88–95.9%, the reaction condition and product characterization are shown in Table 2.

Typical Example. A mixture of (5.69 g; 0.02 mol) of stearic acid (I_d) and (1.74 g; 0.02 mol) of morpholine were dissolved in 50 ml dry toluene in presence P-toluene sulphonic acids (0.0148 g, 0.2 wt%) as catalyst. The mixture was refluxed for seven hours, the solvent (toluene) was evaporated completely, the crude product was separated and purified with diethyl ether; the yield percentage was 88% (see Table 2).

2.2.2. Synthesis of Ferrosurfactant Compounds (III_{a-d})

General Procedure. Mixture of (0.012 mol) of morpholin-4-yl-alkan-1-one (II_{a-d}) and (0.0079 mol) of ferric chloride anhydrous were dissolved in 50 ml of ethanol. The reaction mixture was heated under reflux for 72 hours, the solvent was completely evaporated, and the crude products (III_{a-d}) were separated and purified from proper solvent; the reaction condition and product characterization are shown in Table 3.

Typical Example. A mixture of (4.24 g; 0.012 mol) morpholin-4-yl-octadecan-1-one (II_d) and (1.29 g; 0.0079 mol) of Ferric chloride anhydrous were dissolved in 50 ml of ethanol. The mixture was refluxed for 72 hours. the solvent (ethanol) was evaporated completely, the crude product was separated and purified with diethyl ether; the yield percentage was 86.9% (see Table 3).

This study belongs to the most important category of surface active materials, which named cationic surfactant. There are different types of the cationic surfactant, our study concerning only with metalosurfactants where the synthesis of the compounds occurred in two main steps.

The reaction was procedure according the Scheme 1.

TABLE 1
Chemical used throughout our investigation

Source	Molecular weight	Molecular formula	Materials
Merck	200.3	$C_{12}H_{24}O_2$	Dodecanoic acid
Merck	228.4	$C_{14}H_{28}O_2$	Tetradecanoic acid
Merck	256.4	$C_{16}H_{32}O_2$	Hexadecanoic acid
Merck	284.5	$C_{18}H_{36}O_2$	Octadecanoic acid
Morgan	087.1	C_4H_9NO	Tetrahydro-1,4-oxazine
Aldrich	172.5	$C_7H_8SO_3$	P- Toluene sulphonic acid
Merck	162.5	$FeCl_3$	Ferric chloride

2.3. Confirmation of the Chemical Structure

The structure confirmation of prepared compounds was done through the following spectroscopic techniques: infrared spectra, proton nuclear magnetic resonance (^{1}H NMR), and elemental analysis.

The analyses were carried out at the Micro Analytical Center, Faculty of Science Cairo University.

2.4. Evaluation Methods of Surface Active Properties

2.4.1. Surface Tension Measurements (γ)

Surface tension measurements of the prepared surfactants were made at 25, 35, and 45°C with Du Nouy tensiometer (Kruss type 8451) by using distilled water solution of 0.1% weight concentration.[22] The surface tension of the used distilled water was 72 mN/m at 25°C. Three reading were made on each sample to determine any change with time and to obtain an average value.[23]

2.4.2. Critical Micelle Concentration

The CMC of the prepared surfactants were determined by the surface tension method.[24]. In this method, the surface tension values of the aqueous solutions of the prepared surfactants were plotted versus the corresponding concentrations.

2.4.3. Efficiency (PC20)

The efficiency (PC_{20}) was determined as the concentration (mol/dm^3) capable of suppressing the surface tension by 20 dyne/cm.[25] The efficiency was determined by extrapolating from $\gamma = 52$ to the linear portion before CMC of the versus log C plot, at 25, 35, and 45°C.

2.4.4. Effectiveness (π_{cmc})

The surface tension values at CMC (γ_{cmc}) were used to calculate the values of surface pressure (effectiveness), using the following expression, where γ^o is the surface

TABLE 2
Reaction conditions and product characterizations of fatty acid amide products ($II_{a–d}$)

Yield %	Color	Products (g, mol)	Reaction time (h)	Morpholine (g, mol)	Fatty acids (g, mol)	Comp.*
95.93	Yellowish	(5.67, 0.019)			(4.00, 0.02)	I_a
94.43	Cream	(5.60, 0.018)	7.0	(1.74, 0.02)	(4.56, 0.02)	I_b
91.85	White	(5.98, 0.018)			(5.12, 0.02)	I_c
88.00	White	(6.22, 0.017)			(5.69, 0.02)	I_d

*I_a = lauric acid , I_b = myristic acid , I_c = palmitic acid and I_d = stearic acid.

tension values for purified water at the appropriate temperature and γ_{cmc} is the surface tension at CMC. The effectiveness of adsorption is an important factor that determines such properties of the surfactant as foaming, wetting, and emulsification.[26]

2.4.5. Maximum Surface Excess (Γ_{max})

The surface excess concentration is defined as 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. Γ_{max} were calculated from Gibb's adsorption equation (Equation (1)).

$$\Gamma_{max} = 1/3 \times 2.303RT(\delta\gamma/\delta \log C) \quad [1]$$

where R = 8.314 Jmol-1 K-1, T is absolute temperature, ($\delta\gamma/\delta$ log C) is the slope of the γ versus log C plot at constant temperature.[27] A substance which lowers the surface tension is thus present in excess at or near the surface, that is, when the surface tension decreases with increasing the activity of the surfactant, Γ_{max} is positive.

2.4.6. Minimum Surface Area (A_{min})

A_{min} is the minimum area per molcule of the prepared compounds at the interface and was calculated from the following Equation (2):

$$A_{min} = 10^{14}/N_A\Gamma_{max} \quad [2]$$

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

2.4.7. Standard Free Energies of Micellization ΔG_{mic} and Adsorption ΔG_{ads}

Understanding the process of micellization and adsorption are important for explaining 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. Adsorption and micellization processes of surfactant molecules are considered as phase transformation either from single state molecule in the solution into adsorbed molecules at the interface (adsorption) or into the well aggregated molecules in the form of micelles (micellization).

The thermodynamic parameters of adsorption and micellization of the synthesized cationic surfactants were calculated according to Gibb's adsorption equations as follows:

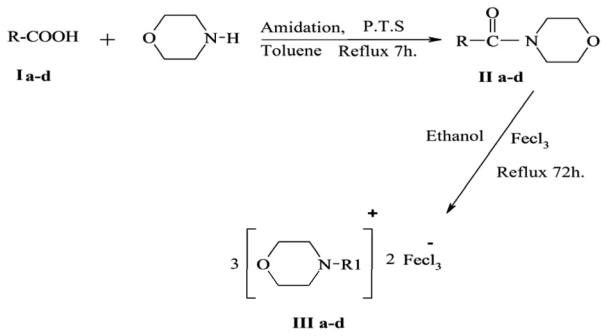
$\Delta G_{mic} = 2.303RT \log (CMC)$
$\Delta G_{ads} = \Delta G_{mic} – (0.6023 \times 10^{-1} \text{ X } \pi_{cmc} \text{ X } A_{min})$
$\Delta S_{mic} = \Delta G_{mic}/T$
$\Delta S_{ads} = \Delta G_{ads}/T$
$\Delta H_{mic} = \Delta G_{mic} + T\Delta S$
$\Delta H_{ads} = \Delta G_{ads} + T\Delta S$

2.5. Measurement of Antimicrobial Activity Using the Diffusion Disc Method

A sterilized disc of filter paper saturated with a measured quantity of the sample is placed on a cavity in plate

TABLE 3
Reaction conditions and product characterizations of ferro-surfactant compounds

Yield %	Color	Products comp. (g, mol)		Time of reaction (h)	Ferric chloride (g, mol)	Morpholin-4-yl-alkan-1-one (g, mol)	Comp.
94.4	Yellow	(4.27, 0.0037)	IIIa			(3.23, 0.012)	II_a
92.3	Dark brown	(4.49, 0.0036)	IIIb			(3.57, 0.012)	II_b
89.9	Brown	(4.67, 0.0035)	IIIc	72	(1.29, 0.0079)	(3.90, 0.012)	II_c
86.9	Chocolate	(4.81, 0.0034)	IIId			(4.24, 0.012)	II_d



where

R1	R	Comp.
CH_3-$(CH_2)_{10}$-CO	CH_3-$(CH_2)_{10}$-	a
CH_3-$(CH_2)_{12}$- CO	CH_3-$(CH_2)_{12}$-	b
CH_3-$(CH_2)_{14}$- CO	CH_3-$(CH_2)_{14}$-	c
CH_3-$(CH_2)_{16}$- CO	CH_3-$(CH_2)_{16}$-	d

SCH. 1.

containing a solid bacterial medium (tryptic soy agar) or fungal medium (sabouraud dextrose agar), which has been 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 the inhibitory power of the sample against the particular tested organism.[28–31]

3. RESULTS AND DISCUSSION

3.1. Structure Confirmation

The chemical structure of prepared surfactants was confirmed by different spectroscopic tools FTIR, ^{1}H NMR spectrometry, and elemental analysis.

3.1.1. A: Elemental Analysis

Confirmation of the prepared compounds is given by elemental analysis of the prepared compounds. The data of the elemental analysis are presented in Table 5. They indicate that the found percentage of C, H, N, Cl, and Fe are nearly close to the calculated measurements.

3.1.2. B: FTIR Spectroscopy

Further confirmation of the chemical structure of the prepared compounds was done by FTIR spectroscopy. The infrared spectroscopy was carried out for the prepared compounds after and before the complexation as shown in Figures 6 and 7, it was found that most important function group (carbonyl of amide group) was decrease by complexation. They appear at 1637–1633 cm^{-1} and after complexation appear at 1626–1611 cm^{-1} and also appear two important bands in the finger print region at 585–584 cm^{-1} and 685–581 cm^{-1} before and after complexation, respectively.

TABLE 4
Identification of morpholin-4-yl-alkan-1-one and their cationic ferrosurfactant complex

Name	Chemical formula	Comp. No.
Morpholin-4-yl-dodecan-1-one	$C_{16}H_{31}NO_2$	II_a
Morpholin-4-yl-tetradecan-1-one	$C_{18}H_{35}NO_2$	II_b
Morpholin-4-yl-hexadecan-1-one	$C_{20}H_{39}NO_2$	II_c
Morpholin-4-yl-octadecan-1-one	$C_{22}H_{43}NO_2$	II_d
Tri[morpholin-4-yl-dodecan-1-one]-di[chlorium ferriate] complex	$C_{48}H_{93}N_3O_6Fe_2Cl_6$	III_a
Tri[morpholin-4-yl-tetradecan-1-one]-di[chlorium ferriate] complex	$C_{54}H_{105}N_3O_6Fe_2Cl_6$	III_b
Tri[morpholin-4-yl-hexadecan-1-one]-di[chlorium ferriate] complex	$C_{60}H_{117}N_3O_6Fe_2Cl_6$	III_c
Tri[morpholin-4-yl-dodecan-1-one]-di[chlorium ferriate] complex	$C_{66}H_{129}N_3O_6Fe_2Cl_6$	III_d

TABLE 5
Microelemental analysis of the prepared ferrosurfactants

Cl%		Fe%		N%		H%		C%		
Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Comp.
19.00	18.81	9.78	9.89	3.20	3.71	8.50	8.21	50.50	50.88	III_a
17.12	17.51	9.40	9.21	3.70	3.45	9.10	8.63	53.00	53.28	III_b
16.65	16.38	8.72	8.61	3.60	3.23	8.80	9.00	55.30	55.38	III_c
15.54	15.39	8.10	8.09	2.80	3.03	9.10	9.32	57.80	57.22	III_d

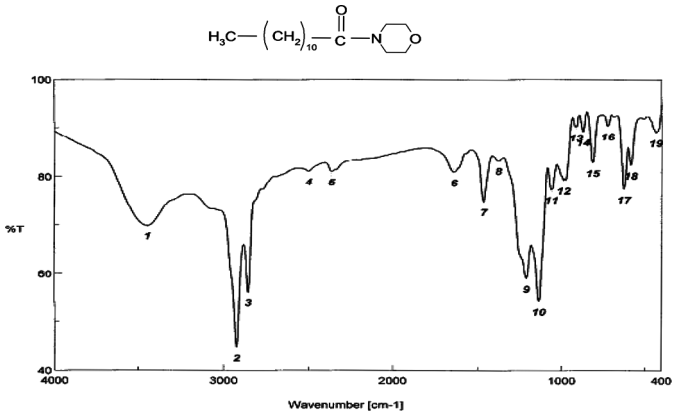


FIG. 1. FTIR spectrum of morpholin-4-yl-dodecan-1-one (II_a).

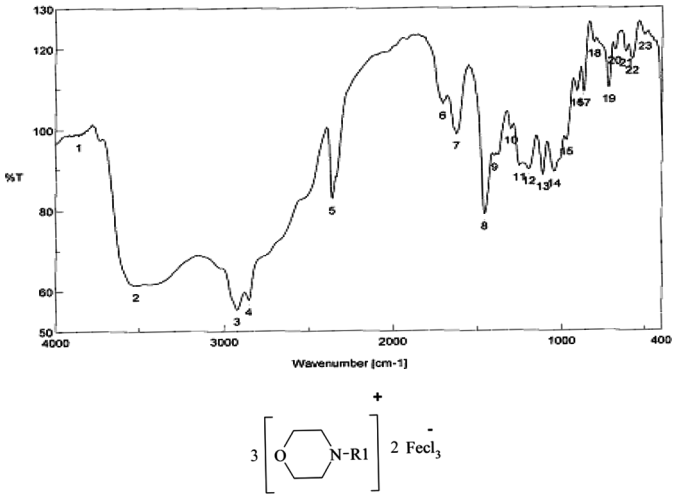


FIG. 2. FTIR spectrum of tri[morpholin-4-yl-dodecan-1-one]-dichloriumferriate] Complex (III_a).

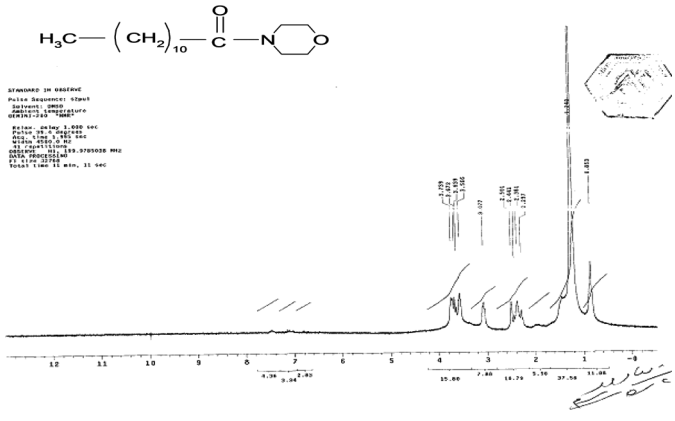


FIG. 3. ^{1}H NMR spectrum of morpholin-4-yl-dodecan-1-one (II_a).

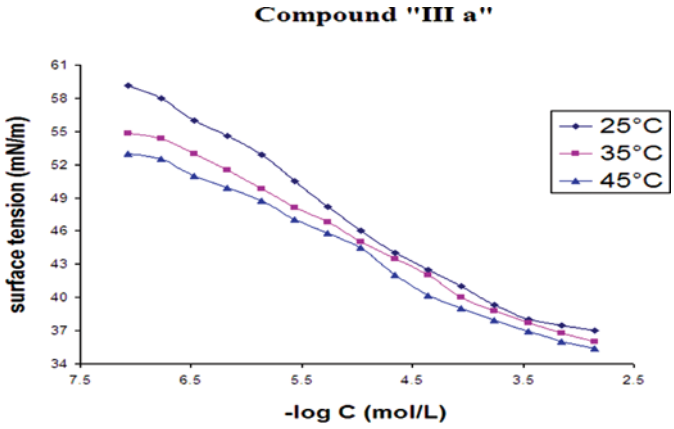


FIG. 4. Surface tension versus–log concentration of complex (IIIa) at different temperatures (25, 35, and 45°C). (Figure available in color online.)

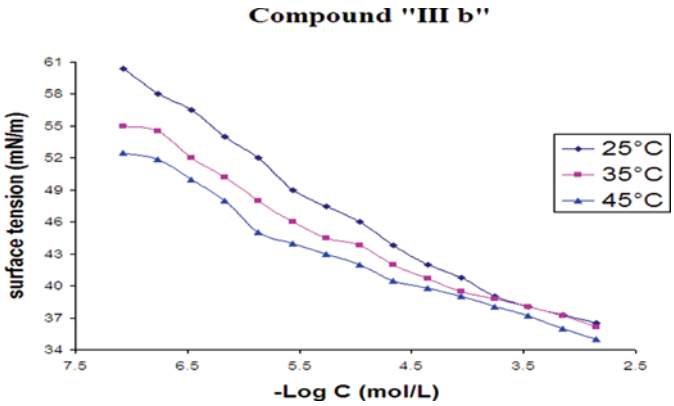


FIG. 5. Surface tension versus–log concentration of complex (IIIb) at different temperatures (25, 35, and 45°C). (Figure available in color online.)

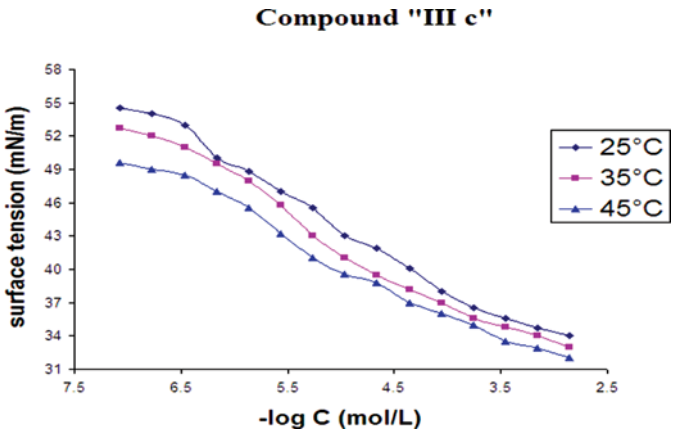


FIG. 6. Surface tension versus–log concentration of complex (IIIc) at different temperatures (25, 35, and 45°C). (Figure available in color online.)

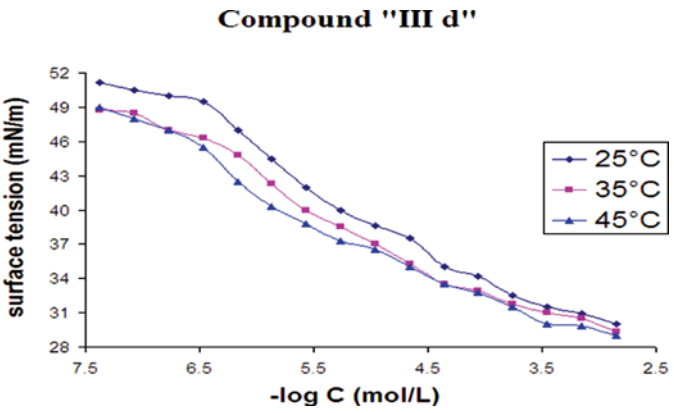


FIG. 7. Surface tension versus–log concentration of complex (IIId) at different temperatures (25, 35, and 45°C). (Figure available in color online.)

3.1.3. C: ^{1}H NMR Spectroscopy

The ^{1}H NMR spectra for prepared compounds are represented as shown in Table 8.

It is clear that all proton types of the products are presents in the charts.

3.2. Surface Parameters

3.2.1. Surface Tensions

The surface tension value of distilled water at 25°C was found to be 72 mN/m and is attributed to the attraction forces between water molecules at the water surface due to the hydrogen bonds. If any foreign molecules are present at the water surface, this leads to disturbance in these forces, leading to a decrease in the surface tension. Surface tension of the prepared cationic ferrosurfactants (III_{a-d}) was measured at 25, 35, and 45°C. The surface tension value of surfactant solutions decrease by increasing the solution concentration as well as by increasing the hydrocarbon chain length and decreases by increasing the solution-temperature, as shown in Figures 4–7. This behavior is due to increase the hydrophobic chain length which leads to decrease in the aqueous solubility and increase the migration of the surfactant molecules from the bulk of the solution to the interface.[32]

3.2.2. CMC of the Prepared Surfactants

Surfactants form aggregates of molecules in aqueous solutions or ions called micelles, which are formed when the concentration of the surfactant solute in the bulk of the solution exceeds a limiting value which called CMC.

As shown in Table 9, it is clear that CMC values of prepared compounds decrease as hydrophobic chains length increase of the compound. Also, the CMC values decreases as the solution temperature increase from 25–45°C. This is due to decrease the solubility of surfactants molecules in the water due to the dehydration of the hydrophobic part as the temperature increases.

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

3.2.3. Effectiveness (π_{CMC})

The effectiveness of surfactant solution (π_{CMC}) is defined as the difference between the surface tension value of the pure water (γ^o) and the surface tension value of the surfactant solution at the critical micelle concentration (γ_{CMC}) at constant temperature.

Table 9 list the effectiveness (π_{CMC}) of the prepared ferrosurfactants at different temperatures 25, 35, and 45°C.

According to the results of the effectiveness, complex (IIId) was found to be the most effective one at 45°C, it gave 41.66 mN/M; it achieved the maximum reduction of surface tension at CMC.

It was found that the increasing of the hydrophobic chain length decrease the interaction with the water phase and hence decrease the surface tension and increase the effectiveness. Also, by increasing the solution temperature the effectiveness of the surfactant increase for the same compound because the surfactant becomes less soluble

TABLE 6
FTIR spectroscopic analysis of the synthesized compounds (II_{a-d}) before complexation

FTIR bands (cm^{-1})				
IId	IIc	IIb	IIa	Function group
1633 and 584	1634 and 585	1637 and 584	1636.3 and 585	$\upsilon_{C=O}$ of amide
2920–2852	2918–2851	2919–2851	2923–2855	υ_{C-H} aliphatic
1118	1108	1108	1135	υ_{C-O-C}

TABLE 7
FTIR spectroscopic analysis of the synthesized compounds (III_{a-d}) after complexation

FTIR bands (cm^{-1})				
III_d	III_c	III_b	III_a	Function group
1680 and 585	1611 and 582	1612 and 585	1626 and 581	$\upsilon_{C=O}$ of amide
2921–2853	2919–2852	2930–2861	2924–2855	υ_{C-H} aliphatic
1113	1101	1103	1115	υ_{C-O-C}

due to the dehydration of the hydrophobic chain as the temperature increases, so the surface tension values decrease.

3.2.4. *Efficiency (pC_{20})*

Efficiency (pC_{20}) is determined by the concentration (mol/dm^3) of the surfactant solution which capable to reduce the surface tension of their solution by 20 mN/M at a certain temperature. The efficiency values of the synthesized surfactants at different temperatures are shown in Table 9.

The efficiency mainly increases with increasing the hydrophobic chain length. In addition, it increases with increasing the temperature.[33]

TABLE 8
^{1}H NMR spectral data of synthesized compounds (II_{a-d}) before complexation

^{1}H NMR spectra data (δppm)	Compd.
0.8–1.0 (t, 3H) of terminal **CH_3**	**II_a**
1.3–1.6 (m, 18H) of CH_3-**$(CH_2)_9$**-	
3.0–3.2 (t, 2H) of CH_3-$(CH_2)_9$-**CH_2**-	
2.3–2.5 (d, 2H) of two hydrogen of morpholine nucleus adjacent to N atom	
3.5–3.8 (d, 2H) of two hydrogen of morpholine nucleus adjacent to oxygen atom	
0.7–1.0 (t, 3H) of terminal **CH_3**	**II_b**
1.0–1.6 (m,22 H) of CH_3-**$(CH_2)_{11}$**-	
2.8–2.9 (t, 2H) of CH_3-$(CH_2)_{11}$-**CH_2**-	
2.1–2.4 (d, 2H) of two hydrogen of morpholine nucleus adjacent to N atom	
3.3–3.7 (d, 2H) of two hydrogen of morpholine nucleus adjacent to oxygen atom	
0.8–1.0 (t, 3H) of terminal **CH_3**	**II_c**
1.1–1.6 (m, 26H) of CH_3-**$(CH_2)_{13}$**-	
2.8–2.9 (t, 2H) of CH_3-$(CH_2)_{13}$-**CH_2**-	
2.1–2.4 (d, 2H) of two hydrogen of morpholine nucleus adjacent to N atom and	
3.3–3.6 (d, 2H) of two hydrogen of morpholine nucleus adjacent to oxygen atom	
0.8–1.0 (t, 3H) of terminal **CH_3**	**II_d**
1.0–1.4(m, 30H) of CH_3-**$(CH_2)_{15}$**-	
2.5–2.6 (t, 2H) of CH_3-$(CH_2)_{15}$-**CH_2**-	
2.1–2.4 (d, 2H) of two hydrogen of morpholine nucleus adjacent to N atom	
3.4–3.7 (d, 2H) of two hydrogen of morpholine nucleus adjacent to O atom	

3.2.5. *Maximum Surface Excess (Γ_{max})*

The maximum surface excess is expressed as the concentration of surfactant molecules at the interface per unit area. Substance that lowering the surface energy is, thus, present in excess at or near the surface, that is, when the surface tension decreases with increasing activity of surfactant, Γ_{max} is positive. The maximum surface excess increases by increasing hydrophobic chains but decrease by increase the temperature as shown in Table 9.

3.2.6. *Minimum Area Per Moelcule (A_{min})*

The minimum surface area is defined as the area occupied by each surfactant molecule at the air-water interface at the equilibrium of the solution. Values of the minimum surface area (A_{min}) per molecules at the aqueous air/water interface for the prepared complexes at different temperatures 25, 35, and 45°C are presented in Table 9. The minimum surface area (A_{min}) increases by increase the temperature but decrease by increase the number of hydrophobic chains in the synthesized surfactant molecules.

3.2.7. *Thermodynamic Parameters of Micellization and Adsorption*

The thermodynamic parameters of micellization and adsorption of the synthesized cationic surfactants were calculated according to Gibb's adsorption equations. The ΔG^O_{mic}, ΔG^O_{ads}, ΔS_{mic}, ΔS_{ads}, ΔH_{mic}, and ΔH_{ads} of the prepared ferrosurfactants were calculated at different temperatures as 25, 35, and 45°C. The thermodynamic values are listed in Tables 10 and 11.

Negative values of standard free energies of both micellization ΔG^O_{mic} and adsorption ΔG^O_{ads} for the prepared surfactants indicate that the micellization and adsorption

TABLE 9
Surface properties of the synthesized cationic ferrosurfactants at different temperature as 25, 35, and 45°C

A_{min} nm^2	$\Gamma_{max} \times 10^{-11}$ mol/cm^2	pC_{20} mol/dm^3	π_{cmc} mN/m	$CMC \times 10^{-4}$ mol/dm^3	Temp. °C	Comp.
1.97	8.45	6.03×10^{-8}	31.50	7.01	25	III_a
2.11	7.85	6.25×10^{-8}	32.33	6.52	35	
2.29	7.25	6.60×10^{-8}	33.67	4.82	45	
1.94	8.54	3.43×10^{-7}	31.62	6.45	25	III_b
2.07	8.00	4.48×10^{-7}	32.46	6.13	35	
2.21	7.52	5.18×10^{-7}	34.63	3.81	45	
1.84	9.01	1.13×10^{-6}	35.82	5.96	25	III_c
2.04	8.16	1.37×10^{-6}	35.89	5.83	35	
2.08	7.98	1.84×10^{-6}	37.17	3.26	45	
1.67	9.94	1.25×10^{-6}	38.85	5.82	25	III_d
1.88	8.84	1.44×10^{-6}	39.86	5.46	35	
1.97	8.43	1.99×10^{-6}	41.66	3.07	45	

are spontaneous processes. The spontaneous process is contributed to the repulsion forces between the different hydrophobic moieties and the polar solvent.

Hence, as the number of hydrophobic parts increase the tendency of the molecules toward adsorption increase which result increase of the negativity values of ΔG^{O}_{ads}. However, the high negativity values of ΔG^{O}_{ads} showed that the process of adsorption is the most predominant process.

Furthermore, the negativity of the two process indicate that these two process are occurred in the same time with some prefer ability to the adsorption process. Obviously, the prepared cationic surfactants prefer adsorption at air/water interfaces due to high interactions between the hydrophobic chains and the polar medium.

3.3. Antimicrobial Activity of the Prepared Cationic Ferrosurfactants

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 building unit in the cell membrane gives them their hydrophobic character.[34]

The selective permeability of the lipoprotein membrane represents the main function, namely, controlling the

TABLE 10
Thermodynamic parameters of micellization of the synthesized ferrosurfactants

ΔH_{mic} $Kjmol^{-1}$	$\Delta S_{mic} = -\Delta G/T$ $Kjmol^{-1}k^{-1}$	ΔG°_{mic} $Kjmol^{-1}$	Temp °C	Compd.
24.0396	0.1410	−17.9995	25	III_a
24.6619	0.1410	−18.7873	35	
24.6624	0.1410	−20.1968	45	
20.7038	0.1305	−18.2048	25	III_b
21.2679	0.1305	−18.9456	35	
20.7036	0.1305	−20.8149	45	
23.7268	0.1413	−18.4018	25	III_c
24.4676	0.1413	−19.0739	35	
23.7263	0.1413	−21.2283	45	
25.1605	0.1463	−18.4588	25	III_d
25.8383	0.1463	−19.2439	35	
25.1605	0.1463	−21.3848	45	

TABLE 11
Thermodynamic parameters of adsorption of the synthesized ferrosurfactants

ΔH_{ads} $Kjmol^{-1}$	$\Delta S_{ads} = -\Delta G/T$ $Kjmol^{-1}k^{-1}$	ΔG°_{ads} $Kjmol^{-1}$	Temp °C	Compd.
24.6336	0.1555	−21.7287	25	III_a
25.0134	0.1555	−22.9039	35	
24.6344	0.1555	−24.8379	45	
30.5084	0.1758	−21.9064	25	III_b
31.1705	0.1758	−23.0023	35	
30.5087	0.1758	−25.4220	45	
29.9194	0.1754	−22.3761	25	III_c
30.5758	0.1754	−23.4737	35	
29.9194	0.1754	−25.8841	45	
36.6354	0.1979	−22.3685	25	III_d
37.2265	0.1979	−23.7564	35	
36.6352	0.1979	−26.3266	45	

TABLE 12
Microbial inhibition zone of tested complexes in millimeters

Inhibition zone diameter of microorganisms in millimeters				
Aspergillas nigar Mold	*Candida albicans* Yeast	*Escherichia coli* G −ve	*Bacillus sutilus* G +ve	Comp.
0.0	0.0	0.0	0.0	Control water
23.3	24.6	22.5	24.5	III_a
13.2	16.0	20.0	19.5	III_b
12.0	12.0	15.0	19.0	III_c
11.3	11.0	13.5	13.0	III_d

biological reactions in the cell hence, any factor which influences that permeability cause's great damage to the microorganisms, which lead to death. the cationic surfactants have a unique ability to adsorb at interfaces were the pathogenic bacterial cell membrane is predominantly negatively charge as compared to eukaryotic cells.[21] Hence the positive charge of the cationic surfactant facilitates their interaction with the bacterial membrane, which lends them a good biocidal activity toward microorganisms.[35,36]

The adsorptions at the water/cell membrane increase the hydrophobicity of that membrane which, increase its permeability toward the media ingredients. This causes disturbance in biochemical reactions within the cell cytoplasm. The results of antimicrobial activity of the synthesized surfactants against pathogenic bacteria and fungi are recorded in Table 12.

In case of metal complex surfactants, the bioactivity was increased to a higher extent, this due to their tendency toward adsorption to wall of the tested microorganisms.[37,38]

4. CONCLUSIONS

From the obtained results, we can conclude that the introduction of the metal in the cationic surfactants enhancing its surface properties and that the prepared ferrosurfactants show good inhibition properties for microorganisms (bacteria and fungi).

REFERENCES

[1] Murguía, M.C., Cristaldi, M.D., Porto, A., Di Conza, J., and Grau, R.J. (2008) *J. Surf. Deterg.*, 11: 41.
[2] Wçgrzyńska, J. and Chlebicki, J. (2006) *J. Surf. Deterg.*, 9: 221.
[3] Badawi, A.M., El-Marazibanl, M.M., Haroun, B., and Soliman, H. (1983) *Corr. Sci.*, 52: 1169.
[4] Domínguez-Gutiérrez, D., De Paoli, G., Guerrero-Martínez, A., Ginocchietti, G., Ebeling, D., Eiser, E., De Cola, L., and Elsevier, C.J. (2008) *J. Mater. Chem.*, 18: 2762.
[5] Hafiz, A.A. (2005) *Surfact. Deterg.*, 8(2).
[6] Hafiz, A.A. (2008) *Journal of the Iranian Chemical Society*, 5(1).
[7] Kenji, H., Tadashi, I., Toshiki, K., and Hirofusa, S. (1993) *Macromol. Chem. Phys.*, 194: 197.
[8] Narayanasamy, K. and Kannappan, S. (2009) *J. Coord. Chem.*, 62: 3500.
[9] Kunjappu, J.T., Somasundaran, P., and Turro, N.J. (1990) *J. Phys. Chem.* 94: 8464.
[10] Wang, R., Liang Y. and Schmehl, R.H. (1994) *Inorg. Chim. Acta*, 225: 275.
[11] Romualdo-Torres, G., Agricole, B., Mingotaud, C., Ravaine, S., and Delhaes, P. (2003) *Langmuir*, 19: 4688.
[12] Chu, B.W.K. and Yam, V.W.W. (2001) *Chem.*, 40: 3324.
[13] Parera, E., Comelles, F., Barnadas, R., and Suades, J. (2011) *Chem. Commun.*, 47: 4460.
[14] Holmberg, K. (2004) *J. Colloid Interface Sci.*, 274: 355.
[15] Yam, V.W.W., Zhu, B., and Li, N. (2002) *Adv. Mater.*, 14: 719.
[16] Iida, M., Sakai, T., Koine, N., and Kaizaki, S. (1993) *J. Chem. Soc. Faraday Trans.*, 89: 1773.
[17] Chen, B.Z. and Sleiman, H.F. (2004) *Macromolecules*, 37: 5866.
[18] Lippard, S.J. and Beg, J.M. (1994) *Principles of Bioinorganic Chemistry*; University Science Books, Mill Valley, CA.
[19] XXXXXXXXXX. (1991). *Cationic Surfactants: Physical Chemistry*; Marcel Dekker, New York.
[20] McDonnell, G. and Russell, A.D. (1999) *Clin. Microbial. Rev.*, 12: 147.
[21] Oren, Z., Hong, J., and Shai, Y.J. (1997) *Biol. Chem.*, 272: 14643.
[22] Findlay, A. (1963) *Practical Physical Chemistry*, 6th ed.; Longman, London, pp. 92–101.
[23] Hampson, J.W. and Cosnell, D.G. (1996) *J. Am. Oil Chem. Soc.*, 73: 891.
[24] Mohamed, A.S. and Wad, M.M.B.A. (2003) *Mat. Sci. Res. India*, 1: 59.
[25] Badawi, A.M., Mekawi, A.S.M., Mohamed, M.Z., and Khowdairy, M.M. (2007) *J. Cancer Res. Ther.*, 3(4): 198.
[26] Rosen, M.J. (1987) *Surfactants and Interfacial Phenomena*; Wiley, New York, p. 72.
[27] Dianno, D., Talmon, Y., and Zana, R. (1995) *Langmuir*, 11: 1448.
[28] Grayer, R.J. and Harbone, J.B. (1994) *Photochemistry*, 37: 19.
[29] Irob, O.N., Moo-Young, M., and Anderson, W.A. (1996) *Int. J. Pharmacogn.*, 34: 87.
[30] Jawetz, E., Melnick, J.L., and Adelberg, E.A. (1974) *Review of Medical Microbiology*; Lang Medical, Los Altos, CA.
[31] Muanza, D.N., Kim, B.W., Euler, K.L., and Williams, L. (1994) *Int. J. Pharmacogn.*, 32: 337.
[32] Barry, B.W. and El-Eini, D.I. (1976) *J. Colloid Interface Sci.*, 54: 339.

[33] Rosen, M.J. (1987) *Surfactants and Interfacial Phenomena*; Wiley, New York.
[34] Przestalski, S., Sarapuk, J., Kleszcznska, H., Habrielska, J., Trela, Z., and Kuczera, J. (2000) *J. Acta Biochem. Polonica*, 47: 627.
[35] Brunt, K. D. (1987) In *Biocides for the Oil Industry*, (edited by H.C. Hill); Wiley, New York, 1987.
[36] Hugo, W. and Snow, G. (1981) *Biochemistry of Antibacterial Action*; Chapman & Hall, London.
[37] Badawi, A.M., Negm, N.A., and El-Zahar, S.M. (2004) *Metal Ions in Biology and Medicine*, 8: 89.
[38] Badawi, A.M., El-Sukkary, M., Aiad, I., El-Sawy, A., and Adawy, A. accepted. *Surf. Deterg.*