"Synthesis and Biological Activity of Some Amide-Based Cationic Surfactant complexes with Co (II) and Cu (II)"

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Abstract: *In this study, different cationic surfactants were prepared by esterfication of different fatty acids with ethanol then amidation of the prepared esters with N, N dimethyl ethylene diamine then quaternized the tertiary amines with benzyl bromide to produce a series of quaternary ammonium salts then preparing of metallocationic surfactants by complexing the cationic surfactants with cobalt chloride and copper chloride.*
Surface tension at different four temperatures of these metallocationic surfactants was investigated. The surface parameters including critical micelle concentration (CMC), maximum surface excess (Γ_{max}), minimum surface area (A_{min}), efficiency (PC_{20}) and effectiveness (π_{CMC}) were studied and the thermodynamic parameters such as free energy of micellization (ΔG^{o}_{mic}) and adsorption (ΔG^{o}_{ads}), enthalpy (ΔH^{o}_{m}), (ΔH^{o}_{ads}) and entropy (ΔS^{o}_{m}), (ΔS^{o}_{ads}) were calculated.
The antimicrobial activity of the prepared complexes was determined via the inhibition zone diameter against different microorganisms also the antimicrobial activity of the prepared complexes against sulfate reducing bacteria (SRB) was determined by the dilution method.
The results indicate that these metallocationic surfactants have good surface properties and good biological activity on broad spectrum of microorganisms.
Key words: *Biological activity, Metallocationic surfactants, Surface parameters.*

I. Introduction

Cationic surfactants of the quaternary ammonium salt type exhibit high surface activity, a strong synergistic effect, good detergency and antimicrobial ability, and are used in the fields of high and novel technology such as new materials manufacture, life science and biotechnology, nano-materials and so on [1–3]. They have been examined for their surface and solution behavior using variety of methods. [4-13].
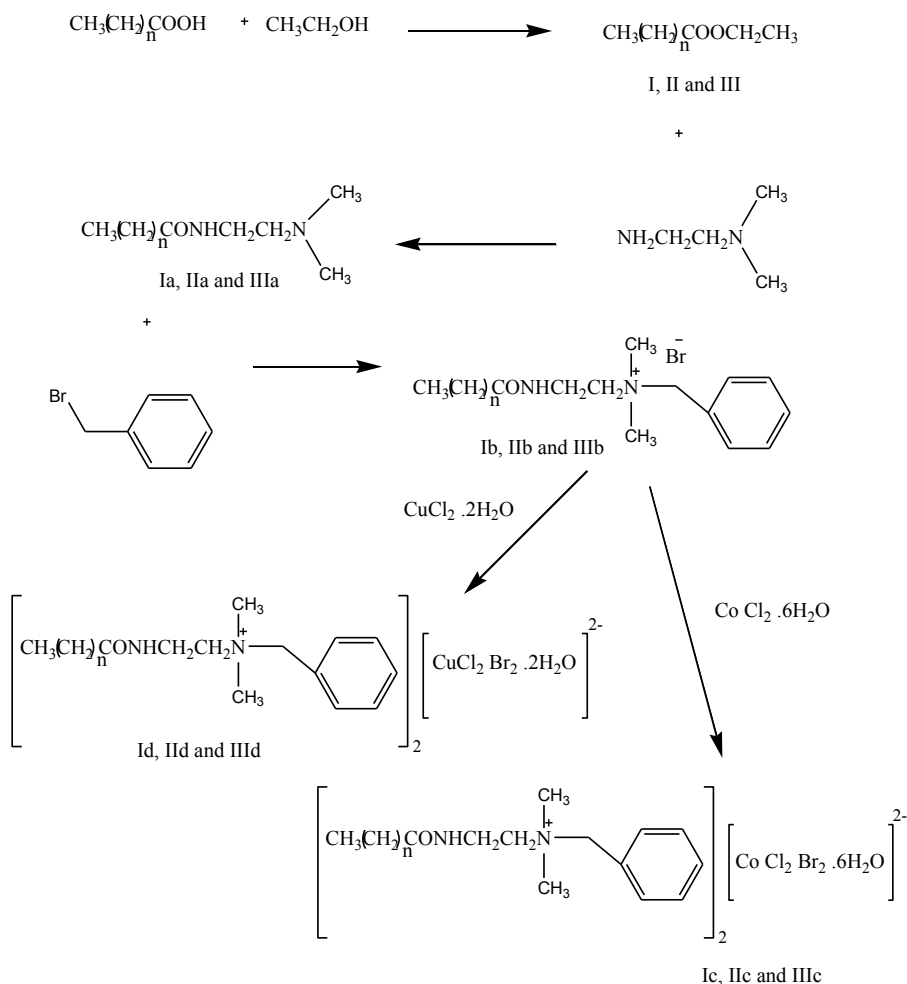
There is a serious problem represented in the microbial resistance to the antibiotics so it is very important to discover novel active compounds against new targets. Many of the crude drugs, which are sources of medicinal preparations, still originate from wild growing material. In this order, developments are done to produce new antibiotics to resist the growth of the different bacterial genera [14, 15].

Available information on cationic surfactants that carry the amide head group is focused on the synthesis and the biological activity of commercial products, i.e., where the tail is a mixture of hydrocarbon groups [16]. This prompted us to start a systematic study on this group of surfactants, in order to understand the relationship between the previously mentioned structural variables and the properties of their aqueous solutions.

In the metallocationic surfactants the metal complex entity containing the central metal ion with its primary coordination sphere acts as the head group and the hydrophobic entity of one or more ligands acts as the tail part.

There are but a few reports of the synthesis, isolation and characterization of surfactant transition metal complexes, in contrast to numerous reports of the formation and study of such surfactants in solution without isolation [17]. It is argued that the high charge and size of the head group of the complex having long paraffin tails, detergent-like characteristics are able to penetrate biological membranes and destabilize the exterior membrane of the organism [18, 19].

In this paper we reported the synthesis and characterization of some novel metallocationic surfactants that used as biocides.

$$CH_3(CH_2)_n COOH \quad + \quad CH_3CH_2OH \longrightarrow CH_3(CH_2)_n COOCH_2CH_3$$

I, II and III

+

$$CH_3(CH_2)_n CONHCH_2CH_2N(CH_3)_2 \longleftarrow NH_2CH_2CH_2N(CH_3)_2$$

Ia, IIa and IIIa

+

$$CH_3(CH_2)_n CONHCH_2CH_2N^+(CH_3)(CH_2C_6H_5)(CH_3) \; Br^-$$

Ib, IIb and IIIb

CuCl₂ .2H₂O

Co Cl₂ .6H₂O

$$\left[CH_3(CH_2)_n CONHCH_2CH_2N^+(CH_3)(CH_2C_6H_5)(CH_3) \right]_2 \left[CuCl_2 Br_2 .2H_2O \right]^{2-}$$

Id, IId and IIId

$$\left[CH_3(CH_2)_n CONHCH_2CH_2N^+(CH_3)(CH_2C_6H_5)(CH_3) \right]_2 \left[Co Cl_2 Br_2 .6H_2O \right]^{2-}$$

Ic, IIc and IIIc

Scheme 1: Preparation of metallocationic surfactants
n = 10 (I : Id), 12 (II : IId) and 14 (III : IIId)

II.   Experimental Procedure

2.1. Materials:
The chemicals used in this study were of pure grade from Aldrich and were used without further purification. The solvents used were of pure grade.

2.2. Synthesis:
1. Synthesis of comounds (I, II and III) were by esterfication of different fatty acids; dodecanoic acid, teradecanoic acid and hexadecanoic acid with ethanol in presence of few amounts of sulfuric acid as dehydrating agent and after the reaction had completed, the solution neutralized by sodium bicarbonates, see scheme (1).
2. Amidation of esters (I, II and III) was by adding one mole of N, N dimethyl ethylene diamine drop wise with stirring in about 30 minutes to one mole of ester then refluxed for about 2 hours to obtain amides (Ia, IIa and IIIa).
3. Quaternization of different amides that containing tertiary nitrogen atom by adding one mole of amides (Ia, IIa and IIIa) to one mole of benzyl bromide in anhydrous acetonitril for twelve hours to produce cationic surfactants quaternary ammonium compounds (Ib, IIb and IIIb).
4. Synthesis of metal complexes (metallosurfactants) were by refluxing of two moles of cationic surfactants (Ib, IIb and IIIb) once with one mole of cobalt chloride (CoCl₂ .6H2O) in acetonitril for four hours to obtain metal complexes (Ic, IIc and IIIc), respectively. And another time with one mole of copper chloride (CuCl₂ 2 H₂O) in acetonitril for four hours to obtain metal complexes (Id, IId and IIId). The reaction mixtures were left to cool then filtered.

2.3. Structural confirmations of the prepared compounds:

The chemical structure of the synthesized compounds was characterized by: FTIR spectra that were obtained using ATI Mattsonm Infinity series[TM], Bench top 961 controlled by Win First[TM] V2.01 software. (Egyptian Petroleum Research Institute).

2.4. Evaluation method of surface active properties:

2.4.1. Surface tension:

Surface tension of the prepared compounds solutions were measured using Du-Nouy Tensiometer (Kruss type 6). The surface tension of different concentrations range of 0.04 to 1.9×10^{-5} mole/liter at different temperature (25, 35, 45 and 55 ^{o}C) was measured.

2.4.2. Surface parameters of the prepared compounds:

a) Critical micelle concentration (CMC):

The values of the critical micelle concentration of the prepared compounds were determined using surface tension technique. Values of the surface tension measurements were plotted against the corresponding concentrations. The interrupt change in the SC curves express on the CMC concentrations.

b) Effectiveness (π_{CMC}):

π_{CMC} is the difference between the surface tension of the pure water (γ_o) and the surface tension of the surfactant solution (γ) at the critical micelle concentration.

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

c) Efficiency (PC_{20}):

Efficiency (PC_{20}) is determined by the concentration (mol/liter) of the surfactant solutions capable to suppress the surface tension by 20 mN/m.

d) Maximum surface excess Γ_{max}:

The values of the maximum surface excess Γ_{max} calculated from surface or interfacial data by the use of Gibbs equation [20].

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

Where

Γ_{max} maximum surface excess in mole/cm^2

n   The number of solute species whose concentration at the interface changes with change in the value of C equal to 2 for conventional ionic surfactants

R   universal gas constant 8.31×10^7 ergs mole^{-1} K^{-1}

    T   absolute temperature ($273.2 + ^{o}$C)

    $\delta \gamma$ surface pressure in dyne/cm

    C   surfactant concentration

    $(\delta \gamma / \delta \log C)_T$ is the slope of a plot surface tension vs. –log concentration curves below CMC at constant temperature.

e) Minimum surface area (A_{min}):

The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule. The average area (in square angstrom) occupied by each molecule adsorbed on the interface [21] is given by:

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

    Γ_{max} maximum surface excess in mole / cm^2

    N   Avogadro's number 6.023×10^{23}

f) Thermodynamic parameters of micellization and adsorption:

The thermodynamic parameters of adsorption and micellization of the synthesized cationic surfactants were calculated according to Gibb's adsorption equations as follows[22]:

$$\Delta G^O_{mic} = RT \ln (CMC)$$
$$\Delta G^O_{ads} = \Delta G^O_{mic} - 6.023 \times 10^{-1} \times \pi_{CMC} \times A_{min}$$
$$\Delta S_{mic} = - d (\Delta G^O_{mic} / \Delta T)$$
$$\Delta S_{ads} = - d (\Delta G^O_{ads} / \Delta T)$$
$$\Delta H_{mic} = \Delta G^O_{mic} + T \Delta S_{mic}$$
$$\Delta H_{ads} = \Delta G^O_{ads} + T \Delta S_{ads}$$

2.4.3. Antimicrobial activity of the prepared compounds:

a. The antimicrobial activity of the prepared metallocationic surfactants was measured individually against a wide range of microorganisms previously isolated in Biotechnology Lab. in Egyptian Petroleum

Research Institute (EPRI) from different oil polluted environments using dose equal to 5 mg/ml by the diffusion agar technique.

The tested compounds were evaluated against Gram -ve bacteria (Escherichia coli and Bordetella pertussis), Gram +ve bacteria (Bacillus subtilis, Micrococcus luteus) and Yeast (Candida albicans) and Filamentous Fungus (Aspergillus niger). The bacteria and yeast were grown on nutrient agar while the fungus was grown on   Czapek`s Dox agar medium.

The negative control was DMF showed no antimicrobial activity against the tested microorganism and the positive control was Erythromycin for bacteria and Metronidazole for yeast and fungus.

All examinations were done in duplicates and the listed data are the average of the obtained results.
b. The antimicrobial activity of the synthesized compounds at 5000 ppm was measured against sulfate reducing bacteria (SRB) using dilution method.

III.   Results And Discussion
3.1. Chemical structure:
The chemical structure of the prepared cationic surfactants was confirmed by FTIR spectra.

3.1.1. FTIR spectra:
The FTIR spectra of the synthesized compounds showed the following absorption bands at 2853.09 – 2857.22 cm^{-1} for CH_2 group, 2924 – 2926.56 cm^{-1} for N^+ group and 3411.67 – 3577.2 for N-H stretch band of amide group, see figs (1-6). The FTIR spectra confirmed the expected functional groups in the synthesized cationic surfactants.

3.2. Surface properties:
3.2.1. Surface tension:
The surface tension was measured for aqueous solutions of the prepared metallocationic surfactant with different concentrations (0.04 to 1.9X 10^{-5} mole/liter) and at different temperatures 25, 35, 45 and 55 ^oC. And the data are represented in surface tension-concentration curves as shown in figures (7-10). It is clear that surface tension decrease by increasing the concentration of the metallocationic complexes due to increasing the migration of the surfactant molecules from the bulk to the interface of the solution, also the figures showed that the surface tension values decrease as the temperature increase from 25 to 55 ^oC and this is because as the temperature increases the surfactants become less soluble due to dehydration of the hydrophobic chain from the solution directed to the surface.

It is expected that the surface tension values of the cationic complexes (Ic, Id, IIc, IId, IIIc and IIId) have lower values than the parent cationic surfactants (Ib, IIb and IIIb). This is due to the increase in the hydrophobicity of these complexes in comparison to the parent cationics, which is due to the presence of two ligands coordinated to the metal ion [23] , i.e., increase the non polar part. Then the water/surfactant molecules interactions increased, which forced them to the air-water interface [24]. so, the surface tension decreased.

3.2.2. The critical micelle concentration (CMC):
Critical micelle concentration values of the prepared metallocationic surfactant were determined by plotting the surface tension (γ) of surfactant solutions versus their bulk concentrations in mole/liter at 25°C, 35°C, 45°C and 55°C. The CMC values are listed in the Tables (1-4) showing a decrease in the CMC with increasing the alkyl chain length, this is because as the alkyl chain length increases the repulsion force in the bulk of the solution increases too which forced the surfactant molecules to the surface and the solution needs less molecules to reach the equilibrium state , i.e., formation of micelles.

Also the CMC decreases as the temperature increases due to the rise of temperature probably decreases in the hydration of the hydrophilic group, which favor micellization. On the other hand, the rise of temperature causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, determines whether the CMC increase or decrease over a particular temperature range. From the data in the Tables (1-4) reveals that CMC decrease upon rising the temperature, i.e, micellization is enhanced.

3.2.3. Effectiveness (Π$_{CMC}$):
The most efficient surfactant is one that gives the greatest lowering in surface tension for a critical micelle concentration (CMC).

According to the results of the effectiveness shown in Tables (1-4) increasing the alkyl chain length and the temperature increase the effectiveness of the complexes due to increase the hydrophobicity. Complexes (IIIc and IIId) were found the most effective ones at 25 °C, it gives 29 and 28 mN/m respectively; it achieved the maximum reduction of surface tension at (CMC). While they achieved the most effective ones at 35 °C, they

give 30 and 29 mN/m respectively. They were the most effective ones at 45 °C, they give 31 and 30 mN/m respectively and they also were the most effective ones at 55 °C, they give 32 and 31 mN/m respectively.

3.2.4. Efficiency (Pc$_{20}$):

Efficiency values of the prepared cationic surfactants are given in the Tables (1-4). From these data it was observed that; when the length of the alkyl chain and the temperature increase, the efficiency decreases due to fast formation of mono layer of surfactants on the surface.

3.2.5. Maximum surface excess (Γ$_{max}$):

The values of Γ$_{max}$ are represented in Tables (1-4). In general maximum surface excess Γ$_{max}$ increases by increasing carbon chain length due to increase the repulsion forces with the water phase so the surfactant molecules migrated to the interface.

3.2.6. Minimum surface area (A$_{min}$):

The minimum area per molecule at the water/air interface for the prepared surfactants is listed in Tables (1-4). The minimum surface area (A$_{min}$) decreases with an increase in the chain length of the hydrophobic part in the surfactant molecules due to the higher accumulation of these molecules at the interface and a smaller available area per molecule.

3.2.7. Standard free energies of micellization and adsorption (ΔG$^o_{mic}$, ΔG$^o_{ads}$):

As shown in the Tables (5-12), the values of ΔG$_{mic}$ and ΔG$_{ads}$ are always negatives indicating these two processes are spontaneous; however, there is a greater increase in the negative value of ΔG$_{ads}$ compared to those of micellization. This suggests the tendency of the molecules to be adsorbed at the interface.

3.3. Antimicrobial activity of the prepared compounds:

The cell membrane of microorganisms is composed of several lipids and protein layers arranged together in specific arrangement called the bilayer (or multilayer lipoprotein structure). The presence of the lipids as a building unit in the cell membrane gives them their hydrophobic character [25].

From the relation between the hydrophobic chain lengths and the antimicrobial activities of the tested compounds Ic, IIc, IIIc, Id, IId and IIId, once can explain that their action mode is the diffusion mechanism [26, 27].

The adsorption tendency of surfactant molecules eases their penetration into the cellular membranes. The charged head groups stabilize that adsorption by the interaction with the negative charges on these membranes. The penetration of the hydrophobic chains into the bacterial or fungal membranes disturbs their selective permeability. That leads to uncontrolled penetration of several components into cellular cytoplasm including the halide ions (surfactant counter ions) which disturbs the biological reactions in these microorganisms and finally causes their death.

1. As shown in the Table (13), the synthesized metallocationic surfactants have moderate activity towards different microorganisms, except compound IIIc gave good activity because it has the longest alkyl chain length.
2. The results of antimicrobial activity of the synthesized biocides against sulfate reducing bacteria (SRB) were determined by dilution method and listed in Table (14). The results indicate that the synthesized metallocationic surfactants have high activity against the tested organisms (SRB).

IV.   Conclusion

The main conclusions of this research present in the following points:
1. The synthesized metallocationic surfactants have good surface activity.
2. The thermodynamic parameters of adsorption and micellization showed the tendency of these compounds toward adsorption at the interfaces and also micellization in the bulk of the solutions.
3. The antimicrobial activity of these compounds was high toward different microorganisms so we can use these novel surfactants as biocides.

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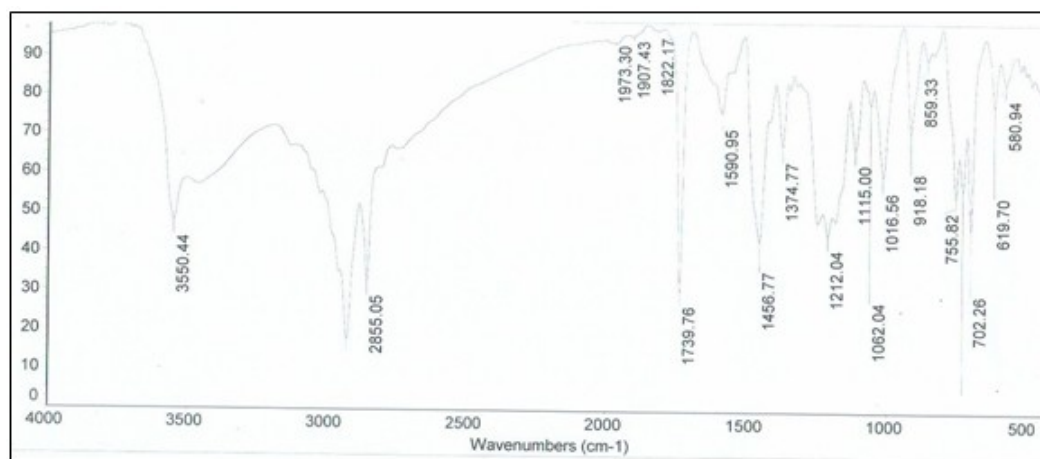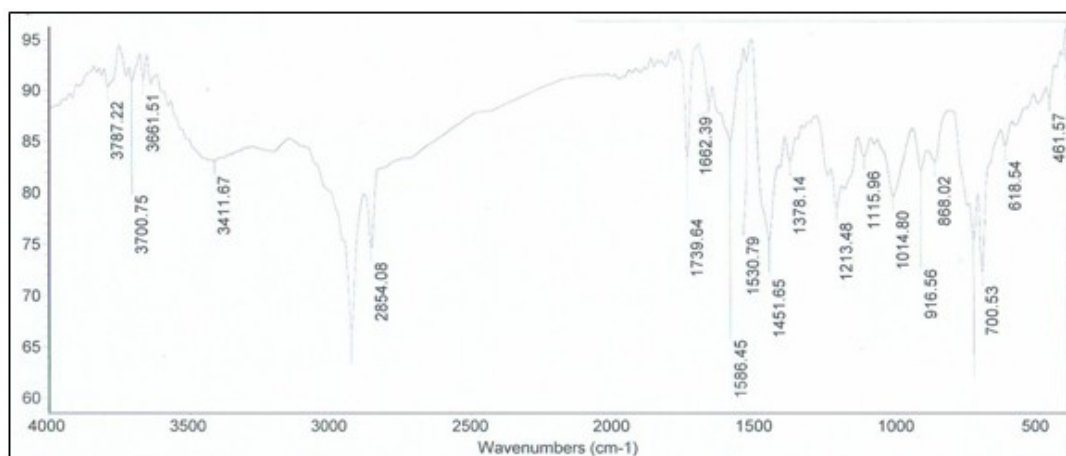
Fig. (1): FTIR spectra of metallocationic surfactant Ic.
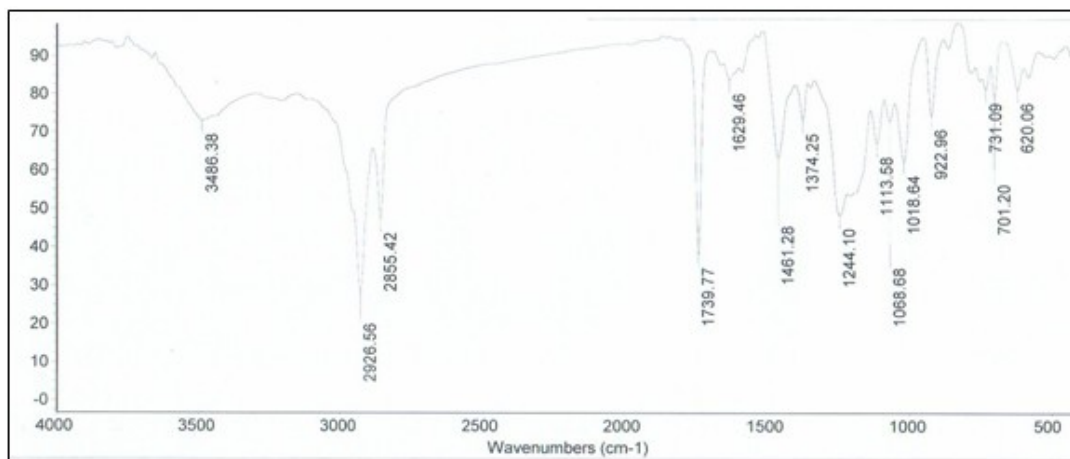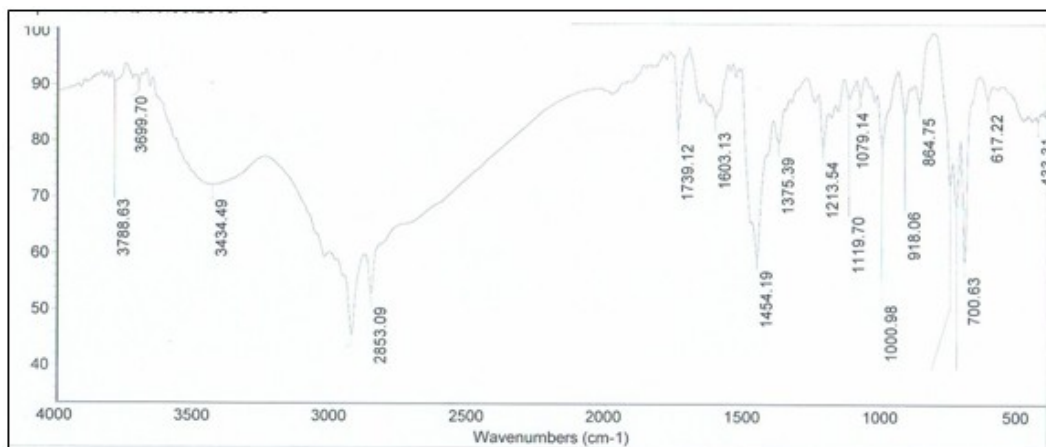
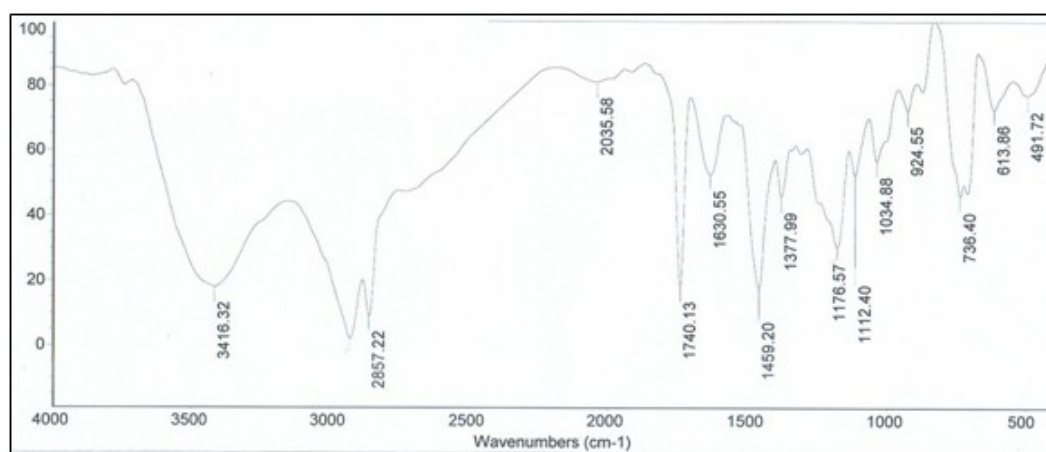**Fig. (2):** FTIR spectra of metallocationic surfactant Id.
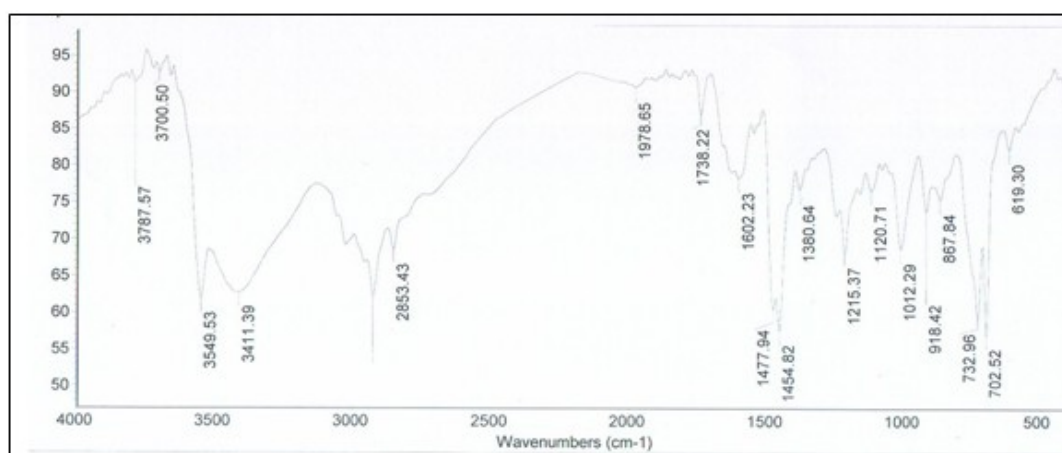
Fig. (3): FTIR spectra of metallocationic surfactant IIc.
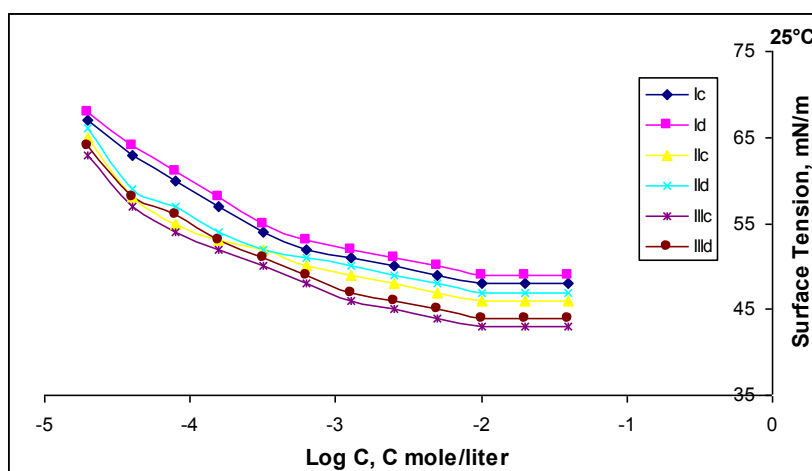

Fig. (4): FTIR spectra of metallocationic surfactant IId.

Fig. (5): FTIR spectra of metallocationic surfactant IIIc.

Fig. (6): FTIR spectra of metallocationic surfactant IIId.

Fig. (7): surface tension versus log concentration of complexes at 25 ^{o}c.
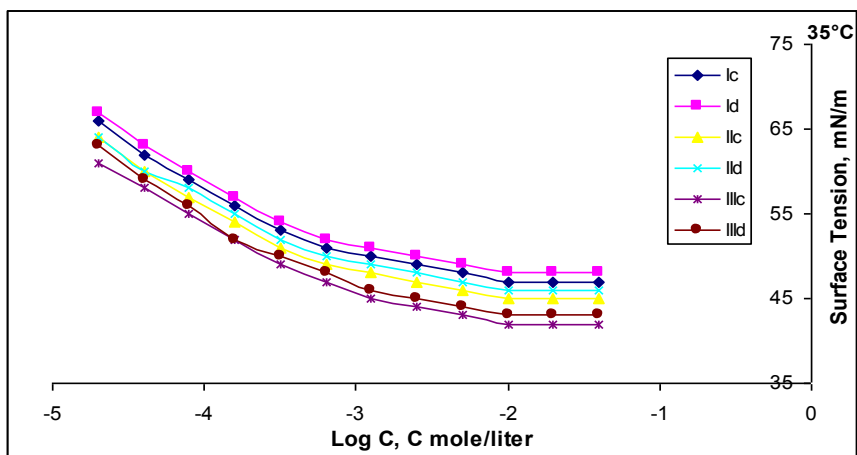
Fig. (8): surface tension versus log concentration of complexes at 35 °c.
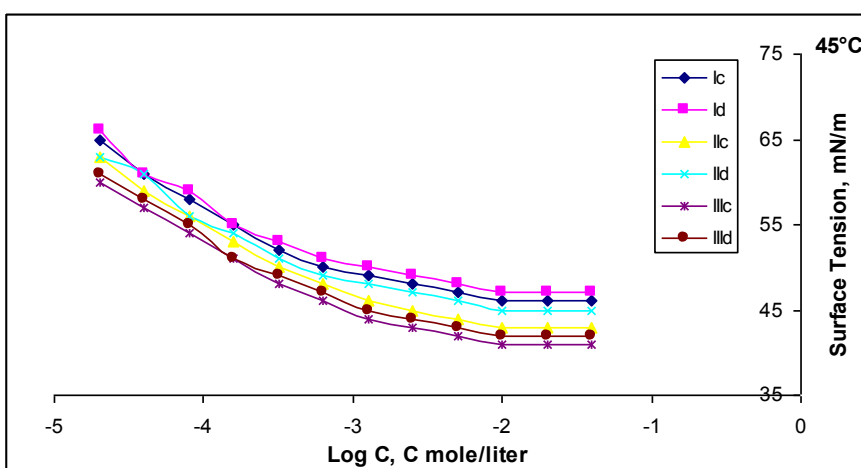
Fig. (9): surface tension versus log concentration of complexes at 45 °c.
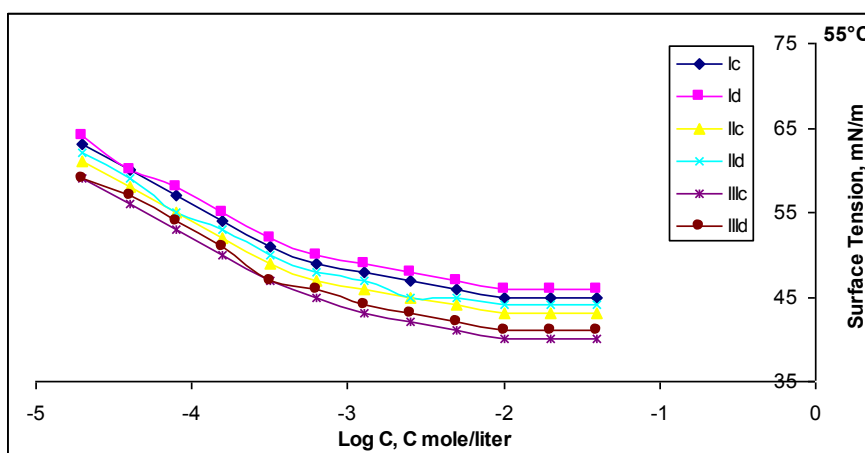
Fig. (10): surface tension versus log concentration of complexes at 55 °c.

Table (1): Surface properties of the synthesized metallocationic surfactants at 25 °C.

Surfactant	CMC X 10^{-3}, mole/liter	π_{CMC}, dyne/cm	Pc$_{20}$ X 10^{-4}, mole/liter	Γ_{max} X 10^{-11}, mole/cm^2	A$_{min}$, nm^2
Ic	1.36	24	6.4	7.94	2.09
Id	1.86	23	12.5	7.94	2.09
IIc	1	26	3.16	7.94	2.09
IId	1.08	25	3.16	8.27	2
IIIc	0.82	29	1.58	8.19	2.03
IIId	0.9	28	2.56	8.27	2

Table (2): Surface properties of the synthesized metallocationic surfactants at 35 °C.

Surfactant	CMC X 10^{-3}, mole/liter	π_{CMC}, dyne/cm	Pc$_{20}$ X 10^{-4}, mole/liter	Γ_{max} X 10^{-11}, mole/cm^2	A$_{min}$, nm^2
Ic	1.19	25	3.77	7.68	2.16
Id	1.44	24	6.3	7.68	2.16
IIc	0.86	27	2.7	8.49	1.96
IId	0.94	26	3.16	7.84	2.12
IIIc	0.73	30	1.58	8.08	2.05
IIId	0.88	29	1.58	8.57	1.94

Table (3): Surface properties of the synthesized metallocationic surfactants at 45 °C.

Surfactant	CMC X 10^{-3}, mole/liter	π_{CMC}, dyne/cm	Pc$_{20}$ X 10^{-4}, mole/liter	Γ_{max} X 10^{-11}, mole/cm^2	A$_{min}$, nm^2
Ic	1.1	26	3.16	7.44	2.23
Id	1.19	25	4.6	7.24	2.29
IIc	0.79	29	2.43	8.22	2.02
IId	0.8	27	2.33	7.98	2.08
IIIc	0.5	31	1.24	8.22	2.02
IIId	0.59	30	1.58	8.49	1.95

Table (4): Surface properties of the synthesized metallocationic surfactants at 55 °C.

Surfactant	CMC X 10^{-3}, mole/liter	π_{CMC}, dyne/cm	Pc$_{20}$ X 10^{-4}, mole/liter	Γ_{max} X 10^{-11}, mole/cm^2	A$_{min}$, nm^2
Ic	1.1	27	2.57	6.93	2.4
Id	1.14	26	3.2	6.74	2.46
IIc	0.63	29	1.6	7.59	2.19
IId	0.69	28	2.03	7.51	2.21
IIIc	0.44	32	7.9	7.97	2.08
IIId	0.54	31	1.58	7.97	2.08

Table (5): Thermodynamic parameters of micellization of the synthesized metallosurfactants at 25 °C.

Surfactant	ΔG^O_{mic}, KJ/mole	ΔS_{mic}, KJ/mole.K	ΔH_{mic}, KJ/mole
Ic	- 16.34	- 0.09	- 42.88
Id	- 15.56	- 0.12	- 50.66
IIc	- 17	- 0.096	- 45.7
IId	- 16.9	- 0.092	- 44.4
IIIc	- 17.6	- 0.08	- 44
IIId	- 17.36	- 0.06	- 36.4

Table (6): Thermodynamic parameters of micellization of the synthesized metallosurfactants at 35 °C.

Surfactant	ΔG^O_{mic}, KJ/mole	ΔS_{mic}, KJ/mole.K	ΔH_{mic}, KJ/mole
Ic	- 17.23	- 0.089	- 44.6
Id	- 16.74	- 0.118	- 53
IIc	- 18.06	- 0.095	- 47.6
IId	- 17.83	- 0.092	- 46.2
IIIc	- 18.48	- 0.089	- 45.8
IIId	- 18	- 0.064	- 37.7

Table (7): Thermodynamic parameters of micellization of the synthesized metallosurfactants at 45 °C.

Surfactant	ΔG^O_{mic}, KJ/mole	ΔS_{mic}, KJ/mole.K	ΔH_{mic}, KJ/mole
Ic	- 18	- 0.056	- 36
Id	- 17.79	- 0.067	- 39.3
IIc	- 18.87	- 0.12	- 57.4
IId	- 18.84	- 0.1	- 50.5
IIIc	- 20.08	- 0.097	- 51
IIId	- 19.64	- 0.08	- 47

Table (8): Thermodynamic parameters of micellization of the synthesized metallosurfactants at 55 °C.

Surfactant	ΔG^O_{mic}, KJ/mole	ΔS_{mic}, KJ/mole.K	ΔH_{mic}, KJ/mole
Ic	- 18.56	- 0.056	- 37
Id	- 18.46	- 0.067	- 40.6
IIc	- 20.08	- 0.12	- 59.8
IId	- 19.83	- 0.099	- 52.5
IIIc	- 21.06	- 0.097	- 53
IIId	- 20.5	- 0.086	- 48.7

Table (9): Thermodynamic parameters of adsorption of the synthesized metallosurfactants at 25 °C.

Surfactant	ΔG^O_{ads}, KJ/mole	ΔS_{ads}, KJ/mole.K	ΔH_{ads}, KJ/mole
Ic	- 46.58	- 0.32	- 142.2
Id	- 44.54	- 0.345	- 147.4
IIc	- 49.86	- 0.001	- 50.2
IId	- 47.13	- 0.386	- 162.1
IIIc	- 53.01	- 0.258	- 129.9
IIId	- 51.21	- 0.063	- 70.1

Table (10): Thermodynamic parameters of adsorption of the synthesized metallosurfactants at 35 °C.

Surfactant	ΔG^O_{ads}, KJ/mole	ΔS_{ads}, KJ/mole.K	ΔH_{ads}, KJ/mole
Ic	- 49.78	- 0.32	- 148.6
Id	- 48	- 0.345	- 154.3
IIc	- 49.87	- 0.001	- 50.3
IId	- 51	- 0.386	- 169.9
IIIc	- 55.6	- 0.258	- 135
IIId	- 51.84	- 0.063	- 71

Table (11): Thermodynamic parameters of adsorption of the synthesized metallosurfactants at 45 °C.

Surfactant	ΔG^O_{ads}, KJ/mole	ΔS_{ads}, KJ/mole.K	ΔH_{ads}, KJ/mole
Ic	- 52.95	- 0.459	- 199
Id	- 52.3	- 0.475	- 203.4
IIc	- 54.15	- 0.415	- 186.3
IId	- 52.65	- 0.444	- 194
IIIc	- 57.8	- 0.342	- 166.6
IIId	- 54.9	- 0.444	- 196.1

Table (12): Thermodynamic parameters of adsorption of the synthesized metallosurfactants at 55 °C.

Surfactant	ΔG^O_{ads}, KJ/mole	ΔS_{ads}, KJ/mole.K	ΔH_{ads}, KJ/mole
Ic	- 57.54	- 0.459	- 208.3
Id	- 57.1	- 0.475	- 213
IIc	- 58.3	- 0.415	- 194.6
IId	- 57.1	- 0.444	- 202.9
IIIc	- 61.2	- 0.342	- 173.4
IIId	- 59.4	- 0.444	- 205

Table (13): The results of the antimicrobial activity of the metallocationic surfactants against tested microorganisms at 5 mg/ml measured by mm.

Test organism / Compuond ID	Bacillus subtilis (+ve)	Micrococcus luteus (+ve)	Escherichia coli (-ve)	Bordetella pertussis (-ve)	Candida albicans (yeast)	Aspergillus niger (fungi)
Ic	22	20	19	18	19	20
Id	19	13	17	16	17	19
IIc	19	22	15	16	18	18
IId	16	-ve	13	15	16	24
IIIc	24	26	20	21	23	17
IIId	15	14	13	17	15	14
Reference	30	32	34	42	25	27

Table (14): Results of Biological activities of tested compounds on mixed culture of Sulfate Reducing Bacterial (SRB) count

Compound ID	SRB/mL
Ic	1.1×10^2
Id	Nil
IIc	Nil
IId	2.1×10^2
IIIc	Nil
IIId	Nil
-ve control	$> 2.4 \times 10^6$