## 2. Result and Discussion

Metal surfactants have various important characters, like physical activities which reduce the surface tension and biological activities where have antimicrobial activities. These surfactants can play as antibacterial and antifungal compounds in pharmaceutical application .Also Metallosurfactants are nowadays having important functions as additives to food and cosmetics.

Metal complex surfactants can synthesized from different starting material compounds as fatty acids and hetero compounds which have many characters used in many field of applications.

This study belongs to the most important category of surface active materials, which named metallocationic surfactant.

The synthesis of these compounds carried out in two main steps:

The first step is preparation of amide compound by reaction of fatty acids as (stearic acid, palmitic acid, myristic acid, lauric acid) with hetero compound as morpholine

The second step is complexation reaction with Fe III which produces ferro metallosurfactants.

#### 2.1. Structure Confirmation:

The chemical structure of prepared surfactants was confirmed by different spectroscopic tools FTIR, <sup>1</sup>H-NMR spectrometry and elemental analysis.

#### 2.1.1. Elemental analysis:

Confirmation of the prepared compounds is given by elemental analysis of the prepared compounds. The data of the elemental analysis are present in Table 1. They indicate that the found percentage of C, H, N, Cl and Fe are nearly close to the calculated measurements.

**Table 1:** The micro elemental analysis of the prepared ferrosurfactants.

Comp	C	%	Н	[%	N	%	Fe	2%	Cl	%
Comp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.
III a	50.88	50.50	8.21	8.50	3.71	3.20	9.89	9.78	18.81	19.00
III b	53.28	53.00	8.63	9.10	3.45	3.70	9.21	9.40	17.51	17.12
III c	55.38	55.30	9.00	8.80	3.23	3.60	8.61	8.72	16.38	16.65
III d	57.22	57.80	9.32	9.10	3.03	2.80	8.09	8.10	15.39	15.54

#### 2.1.2. 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 Table 2 &3, it was found that most important function group (carbonyl of amide group) was decrease by complexation. They was appear at 1637 -1633 cm<sup>-1</sup> and after complexation appear at 1626 -1608 cm<sup>-1</sup> and also appear two important bands in the finger print region at 585 -584 cm<sup>-1</sup> and 585– 581cm<sup>-1</sup> before and after complexation, respectively.

**Table 2:** FTIR spectroscopic analysis of the synthesized compounds (II a-d) Before Complexation.

		FTIR Band	ls (cm <sup>-1</sup> )	
Function group	IIa	IIb	IIc	IId
	c.f.Fig.(14)	c.f.Fig.(15)	c.f.Fig.(16)	c.f.Fig.(17)
$v_{C=O}$ of amide	1636 and 585	1637 and 584	1634 and 585	1633 and 584
υ <sub>C-H</sub> aliphatic	2923-2855	2919-2851	2918-2851	2920-2852
υ <sub>C-O-C</sub>	1135	1108	1108	1118

**Table 3:** FTIR spectroscopic analysis of the synthesized compounds (III a-d) After Complexation.

	FTIR Bands (cm <sup>-1</sup> )					
Function group	IIIa	IIIb	IIIc	IIId		
	c.f.Fig.(18)	c.f.Fig.(19)	c.f.Fig.(20)	c.f.Fig.(21)		
$v_{C=O}$ of amide	1626 and 581	1612 and 585	1611 and 582	1608 and 585		
υ <sub>C-H</sub> aliphatic	2924 -2855	2930 -2861	2919 -2852	2921 -2853		
υ <sub>C-O-C</sub>	1115	1103	1101	1113		

# 2.1.3. <sup>1</sup>H-NMR Spectroscopy:

The <sup>1</sup>H-NMR spectra for prepared compounds are represented as shown in **Table 4**. It's clear that all proton types of the products are presents in the charts.

Compound	<sup>1</sup> H-NMR Spectra data (δppm)
	$0.8-1.0$ (t, 3H) of terminal $\mathbf{CH_3}$
II a	1.3–1.6 (m, 18H) of $CH_3$ -( $CH_2$ ) <sub>9</sub> -
c.f. Fig.(22)	3.0 - 3.2 (t, 2H) of CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>9</sub> -CH <sub>2</sub> -
	2.3–2.5 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to N atom
	3.5–3.8 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to oxygen atom
	0.7 –1.0 (t, 3H) of terminal <b>CH</b> <sub>3</sub>
II b	1.0–1.6 (m,22 H) of CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>11</sub> -
c.f. Fig.(23)	2.8 - 2.9 (t, 2H) of CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>11</sub> - <u>CH</u> <sub>2</sub> -
	2.1–2.4 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to N atom
	3.3–3.7 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to oxygen atom
	0.8–1.0 (t, 3H) of terminal <b>CH</b> <sub>3</sub>
II c	1.1 - 1.6 (m, 26H) of CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>13</sub> -
c.f. Fig.(24)	2.8 - 2.9 (t, 2H) of CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>13</sub> -CH <sub>2</sub> -
	2.1–2.4 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to N atom
	3.3–3.6 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to oxygen atom
	0.8–1.0 (t, 3H) of terminal <b>CH</b> <sub>3</sub>
II d	1.0–1.4(m, 30H) of $CH_3$ -( $CH_2$ ) <sub>15</sub> -
c.f. Fig.(25)	2.5 - 2.6 (t, 2H) of CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>15</sub> -CH <sub>2</sub> -
	2.1–2.4 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to N atom
	3.4–3.7 (d, 4H) of 2 (CH <sub>2</sub> ) hydrogen of morpholine nucleus adjacent to O atom

#### 2.2. Surface Parameters:

The influence of the structure and the molecular weight of the prepared metallosurfactants on the physical properties were assesses. The surface parameters including critical micelle concentration (CMC), efficiency (pC<sub>20</sub>), effectiveness ( $\pi_{cmc}$ ), maximum surface excess ( $\Gamma_{max}$ ) and minimum surface area (A <sub>min</sub>) were studied.

The thermodynamic parameters of micellization is studied as standard free energy ( $\Delta G_{mic}$ ),entroby( $\Delta S_{mic}$ ) and enthalpy( $\Delta H_{mic}$ ).

And also thermodynamic parameters of adsorption as standard free energy  $(\Delta G_{ads})$ , entroby  $(\Delta S_{ads})$  and enthalpy  $(\Delta H_{ads})$ .

#### 2.2.1. Surface tension:

Surface tension is a characteristic property for the liquids and it attributed to the attraction forces between the molecules at the surface. The surface tension value of the distilled water at (25 °C) was found (72 mN/m), which is attributed to the attraction forces between water molecules at the water surface due to the hydrogen bonds. If any foreign molecules present at the water surface leads to disturb that tension and decrease it. Meanwhile, surfactant molecules tend to be adsorbed at the air-water interface at lower concentrations due to the hydrophobic part (non polar phase) which decrease the aqueous solubility due to the repulsion occurred between it and the water molecules (polar phase) and the surfactant molecules forced to migrate from the bulk of the solution to the interface to reduce that repulsion. Hence, by increasing the surfactant concentration, the surface tension of the resulted solution decreases gradually. Longer hydrophobic chains has higher repulsion forces in the water medium, hence, the molecules will tend to adsorb at the interface with high concentrations. Meanwhile, shorter hydrophobic

chains have lower tendency to adsorb at the interface due to the lower repulsion occurred from the aqueous phase. Surfactant metal complexes (Metallosurfactants) are expected to provide a wide range of interesting phenomena on aggregation in aqueous solutions due to variations in charge numbers, size and extent of hydrophobicity through combination of the metal and ligands. Metalloaggregates are made of surfactants that combine a metal-coordinating polar head to hydrophobic tail. The polar head of the surfactant is functionalized with metal ions bound to and surrounded by a hydrophobic region. The surface tension was measured at different concentrations (1.4\*10<sup>-3</sup> to 4.25\*10<sup>-8</sup> M/L) and at different temperatures 25, 35 and 45 °C c.f. Tables (5 -8).

The surface tension values of the synthesized metallosurfactants were plotted against (– log concentration) at different temperatures (25 °C, 35 °C and 45 °C) c.f. Figs. (7-13).

Generally, the drawing Figs. (7-10) showed that:

There are two characteristic regions. One region at lower concentrations, in it the surface tension is greatly sensitive towards concentration variations. The other region at higher concentrations, in it the surface tension is almost constant upon variation of surfactant concentration.

The intersection between the two regions determines the critical micelle concentration (CMC).

At lower concentrations, the surface tension values of the metallosurfactant solutions are high. Increasing the concentration leads to decrease in the surface tension. This decrease can be referred to the accumulation of the surfactant molecules at the interface which disturb the binding forces between water molecules leading to decrease the surface tension to considerable values.

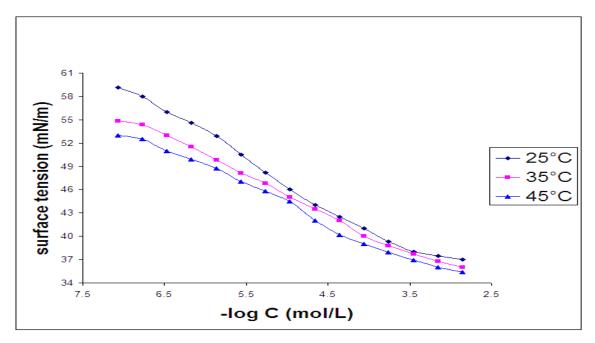
Also, the drawing Figs. (11-13) showed that:

The surface tension values decrease as the temperature increase from 25 °C to 45°C and this is because the surfactants become less soluble due to dehydration of the hydrophobic chain as the temperature increases. The CMC values show a decreasing trend as the temperature increases.

The synthesized surfactants showed a great decrease in the surface tension values by increasing the concentrations. This decrease in the surface tension depends mainly on the hydrophobic chain length and the number of it in each compound of these surfactants and also the presence of the metal ion.

**Table 5:** Surface tension at different Temperatures and different Concentrations of complex (III a)

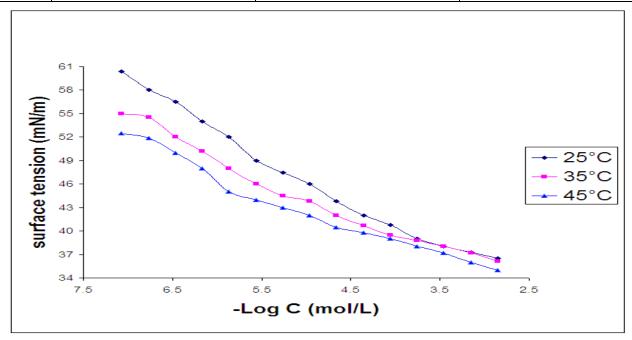
	at 25°C	at 35°C	at 45°C
T 0			
-Log C	Values of surface tension	Values of surface tension	Values of surface tension
	mN/m	mN/m	mN/m
2.8538	37.0	36.0	35.4
3.1549	37.5	36.8	36.0
3.4559	38.0	37.7	36.9
3.7569	39.3	38.8	37.9
4.0579	41.0	40.0	39.0
4.3595	42.5	42.0	40.2
4.6615	44.0	43.5	42.0
4.9625	46.0	45.0	44.5
5.2628	48.2	46.8	45.8
5.5638	50.5	48.1	47.0
5.8664	52.9	49.8	48.7
6.1674	54.6	51.5	49.9
6.4672	56.0	53.0	51.0
6.7695	58.0	54.4	52.5
7.0705	58.0	54.8	53.0



**Fig. (7):** Surface tension vs. – Log Concentration of complex (III a) at different temperatures (25, 35 and 45  $^{\circ}$  C).

**Table 6:** Surface tension at different Temperatures and different Concentrations of complex (III b).

	at 25°C	at 35°C	at 45°C
-Log C	Values of surface tension	Values of surface tension	Values of surface tension
	mN/m	mN/m	mN/m
2.8538	36.5	36.1	35.0
3.1549	37.3	37.2	36.0
3.4559	38.0	38.0	37.2
3.7569	39.0	38.8	38.0
4.0579	40.8	39.5	39.0
4.3595	42.0	40.7	39.8
4.6615	43.8	42.0	40.5
4.9625	46.0	43.8	42.0
5.2628	47.5	44.5	43.0
5.5638	49.0	46.0	44.0
5.8664	52.0	48.0	45.0
6.1674	54.0	50.2	48.0
6.4672	56.5	52.0	50.0
6.7695	58.0	54.5	51.9
7.0705	58.5	55.0	52.5



**Fig. (8):** Surface tension vs. – Log Concentration of complex (III b) at different temperatures (25, 35 and 45  $^{\circ}$  C).

**Table 7:** Surface tension at different Temperatures and different Concentrations of complex (III c)

	At 25°C	At 35°C	At 45°C
-Log C	Values of surface tension	Values of surface tension	Values of surface tension
	mN/m	mN/m	mN/m
2.8538	34.0	33.0	32.0
3.1549	34.7	34.0	32.9
3.4559	35.6	34.8	33.5
3.7569	36.5	35.6	35.0
4.0579	38.0	37.0	36.0
4.3595	40.1	38.2	37.0
4.6615	41.9	39.5	38.8
4.9625	43.0	41.0	39.6
5.2628	45.5	43.0	41.0
5.5638	47.0	45.8	43.2
5.8664	48.8	48.0	45.5
6.1674	50.0	49.5	47.0
6.4672	53.0	51.0	48.5
6.7695	54.0	52.0	49.0
7.0705	54.5	52.7	49.6

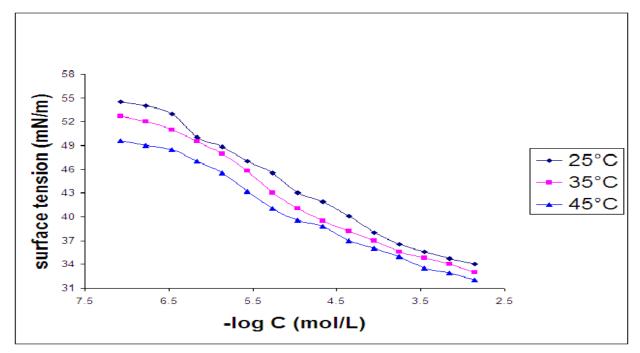
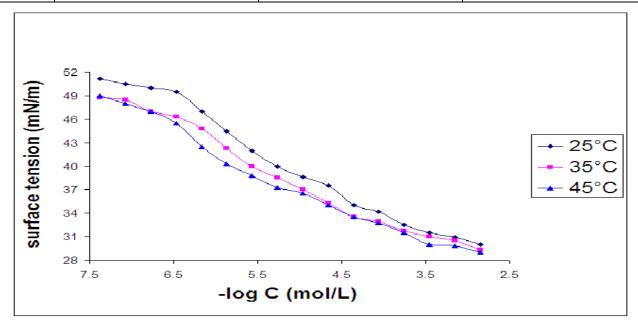


Fig. (9): Surface tension vs. – Log Concentration of complex (III c) at different temperatures (25, 35 and 45  $^{\circ}$  C).

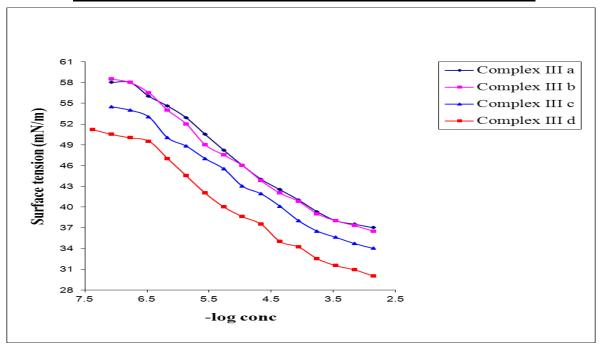
**Table 8:** Surface tension at different Temperatures and different Concentrations of complex (III d)

	At 25°C	At 35°C	At 45°C
-Log C	Value of surface tension	Value of surface tension	Value of surface tension
	mN/m	mN/m	mN/m
2.8538	30.0	29.3	29.0
3.1549	30.9	30.5	29.8
3.4559	31.5	31.0	30.0
3.7569	32.5	31.8	31.5
4.0579	34.2	32.9	32.8
4.3595	35.0	33.5	33.5
4.6615	37.5	35.3	35.0
4.9625	38.6	37.0	36.5
5.2628	40.0	38.5	37.3
5.5638	42.0	40.0	38.8
5.8664	44.5	42.3	40.3
6.1674	47.0	44.8	42.5
6.4672	49.5	46.3	45.5
6.7695	50.0	47.0	47.0
7.0705	50.5	48.5	48.0
7.3716	51.2	48.7	49.0

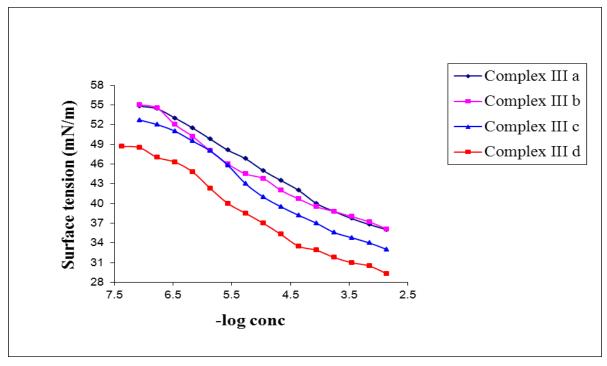


**Fig.(10):** Surface tension vs. – Log Concentration of complex (III d) at different temperatures (25, 35 and 45  $^{\circ}$  C).

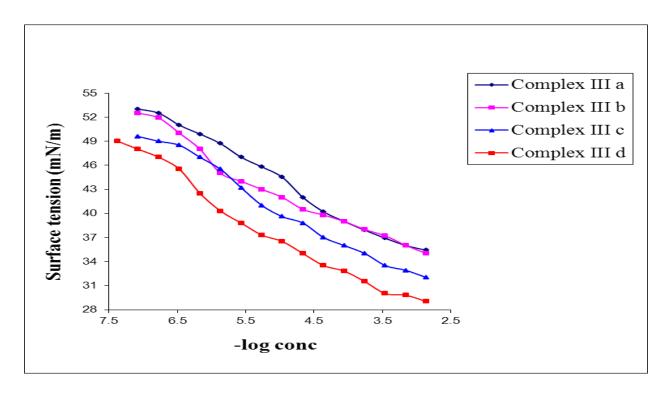
# - These figures show relation between surface tension vs. - Log concentration of all compounds at different temperatures (25, 35, 45 °C).



**Fig. (11):** Surface tension vs. – Log Concentration of compound (III a, III b, III c and III d) at temperatures (25 °C).



**Fig. (12):** Surface tension vs. – Log Concentration of compound (III a, III b, III c and III d) at temperatures (35 °C).



**Fig.(13):** Surface tension vs. – Log Concentration of compound (III a, III b, III c and III d) at temperatures (45 °C).

#### 2.2.2. Critical micelle concentration (CMC)

The critical micelle concentration is defined as the concentration of the surfactant at which no further decrease in the surface tension could be obtained upon addition of any further amounts of surfactant in the solution .

There is equilibrium between the singly adsorbed surfactant molecules at the interface and the micellized surfactant molecules. That equilibrium occurred at the concentration of complete surface saturation (CMC).

The micelle formation is the most vital point of view in the surfactant fundamental because it is the most effective geometric arrangement of the molecules at that desired concentration.

The surfactant molecules when dispersed in the water tend to be adsorbed at the interface, leading to decrease in the surface tension of the surfactant solutions. Further increase in the concentration is followed by gradual reduction of the surface tension until the surface of the solution becomes completely occupied by the surfactant molecules, after that the excess molecules tend to self aggregate in the bulk of the solution to form micelles. Micelle formation or micellization is an important phenomenon because of a number of important interfacial properties such as detergency and solubilization. Critical micelle concentration values of the prepared cationic surfactants have been obtained graphically by plotting the surface tension (γ) in (mN/m) of aqueous solution of the prepared surfactants versus -log concentrations in (mole/liter) at 25°C, 35°C and 45°C. Table 9 lists the critical micelle concentrations (CMC) of the prepared surfactants given from their surface tension at different temperatures 25°C, 35°C and 45°C.

It has shown in the Table 9 that CMC values decrease as the number of hydrophobic chains increase in the same compound.

Which indicate that as the number of hydrophobic chains increase as the surfactant tends to micellize at lower concentration. That can be referred to the high repulsion forces occurred between the surfactant molecules and the aqueous phase. Then, the molecules form aggregates in their solutions at which the polar groups are facing the water phase while the non polar portions located in the middle of these aggregates.

Also, the critical micelle concentration (CMC) values decrease as the temperature increase from 25 °C to 45 °C and this is because the surfactants become less soluble due to the dehydration of the hydrophobic chain as the temperature increases.

#### 2.2.3. Effectiveness ( $\pi_{CMC}$ ):

The effectiveness of surfactant solution  $(\pi_{CMC})$  is defined as the difference between the surface tension of the pure water  $(\gamma_o)$  and the surface tension of the surfactant solution at the critical micelle concentration  $(\gamma_{CMC})$  at constant temperature.

$$\pi_{\text{CMC}} = \gamma_{\text{o}} - \gamma_{\text{CMC}}$$
 .....(3)

Where  $(\gamma_0)$  is the surface tension for pure water at the appropriate temperature and  $(\gamma_{CMC})$  is the surface tension at (CMC).

Above the critical micelle concentration (CMC) the surface tension ( $\gamma$ ) does not change much with the concentration; accordingly, ( $\gamma_{CMC}$ ) used to calculate the values of the surface pressure (effectiveness).

The effectiveness values are considered a good variable in comparison between different surfactants in the same series. The most effective one (in one series of homologous) is that capable to decrease the surface tension at the critical micelle concentration to lower values at constant temperature.

Tables 9 list the effectiveness ( $\pi_{CMC}$ ) of the prepared surfactants at different temperatures 25°C, 35 °C and 45 °C.

According to the results of the effectiveness, complex (III d) was found the most effective one at 45 °C, it gives 41.66 mN/m; it achieved the maximum reduction of surface tension at (CMC).

Increasing the number of hydrophobic chains in the same compound increase the interaction with the water phase and hence decrease the surface tension and increase the effectiveness according to equation (3). Also, by increasing the temperature the effectiveness increase for the same compound because the surfactant becomes less soluble due to the dehydration of the hydrophobic chain as the temperature increases, so the surface tension decrease.

### 2.2.4. <u>Efficiency (Pc<sub>20</sub>):</u>

Efficiency ( $Pc_{20}$ ) is determined by the concentration (Mole/L) of the surfactant solution which capable to reduce the surface tension of their solution by 20mN/m at a certain temperature.

Therefore, the most effective surfactant is the one that gives a surface pressure of 52mN/m at the lowest concentration.

The efficiency is an important parameter concern with the comparison between different homologues of surfactants. The efficiency values of the synthesized surfactants at different temperatures are shown in Table 9.

The efficiency mainly increases with increasing the number of hydrophobic chains in the same compound. In addition, it increases with increasing the temperature.

#### 2.2.5. Maximum surface excess ( $\Gamma_{\text{max}}$ ):

The maximum surface excess is expressed as the concentration of surfactant molecules at the interface per unit area ( $\Gamma_{max}$ ).

The number of surfactant molecules at the air-water interface can be calculated from surface tension values for the prepared surfactants (III a, III b, III c and III d) below the critical micelle concentration at 25°C, 35°C and 45°C according to Gibb's equation:

$$\Gamma_{\text{max}} = -(1/2.303 \text{ RT}) (\delta \gamma / \delta \log C)_{\text{T}}$$
 .....(4)

#### Where

 $\Gamma_{\rm max}$  maximum surface excess in mole/cm<sup>2</sup>

R universal gas constant 8.31 x 10<sup>7</sup> ergs mole<sup>-1</sup> K<sup>-1</sup>

T absolute temperature (273.2 + t)

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

C surfactant concentration

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

The results were listed in Table 9.

A substance which lowers the surface energy is thus present in excess at or near the surface, i.e., when the surface tension decreases with increasing the activity of surfactants, ( $\Gamma_{max}$ ) is positive.

The maximum surface excess increases by increasing temperature and the number of hydrophobic chains due to increase the interaction with the water phase so the surfactant molecules are directed to the interface which decreases the surface energy of the solution.

## 2.2.6. Minimum surface area (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, the average area occupied by each molecule adsorbed on the interface is given by:

$$A_{min} = 10^{16} / \Gamma_{max} N \dots (5)$$

Where

 $\Gamma_{\rm max}$  Maximum surface excess in mole / cm<sup>2</sup>

N Avogadro's number 6.023 x 10<sup>23</sup>

Values of the minimum surface area  $(A_{min})$  per molecules at the aqueous air/water interface for the prepared complexes (III a, III b, III c and III d) at different temperatures 25° C, 35°C and 45 °C are presented in Table 9.

The minimum surface area  $(A_{min})$  decrease with increase temperature and the number of hydrophobic chains in the synthesized surfactant molecules due to the higher accumulation of theses molecules at the interface and hence the area available for each molecule being too small.

**Table 9:** Surface properties of the synthesized cationic ferrosurfactants at different temperature as 25, 35 and 45° C.

Comp.	Temp. °C	CMC×10 <sup>-4</sup> mol/L	π <sub>cmc</sub> mN/m	pC20 mol/L	$\Gamma_{ m max}  imes 10^{-11}$ $_{ m mol/cm^2}$	$A_{\min \atop nm^2}$
	25	7.01	31.50	6.03×10 <sup>-8</sup>	8.45	1.97
III a	35	6.52	32.33	6.25×10 <sup>-8</sup>	7.85	2.11
	45	4.82	33.67	6.60×10 <sup>-8</sup>	7.25	2.29
	25	6.45	31.62	3.43×10 <sup>-7</sup>	8.54	1.94
III b	35	6.13	32.46	4.48×10 <sup>-7</sup>	8.00	2.07
	45	3.81	34.63	5.18×10 <sup>-7</sup>	7.52	2.21
	25	5.96	35.82	1.13×10 <sup>-6</sup>	9.01	1.84
III c	35	5.83	35.89	1.37×10 <sup>-6</sup>	8.16	2.04
	45	3.26	37.17	1.84×10 <sup>-6</sup>	7.98	2.08
	25	5.82	38.85	1.25×10 <sup>-6</sup>	9.94	1.67
III d	35	5.46	39.86	1.44×10 <sup>-6</sup>	8.84	1.88
	45	3.07	41.66	1.99×10 <sup>-6</sup>	8.43	1.97

#### 2.3. 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  $\Delta G^{o}_{mic}$ ,  $\Delta G^{o}_{ads}$ ,  $\Delta S_{mic}$ ,  $\Delta S_{ads}$ ,  $\Delta H_{mic}$  and  $\Delta H_{ads}$  of the prepared ferrosurfactants were calculated at different temperatures as 25, 35 and 45 °C. The thermodynamic values are listed in Tables (10 -11).

Negative values of standard free energies of both micellization  $\Delta G^{o}_{mic}$  and adsorption  $\Delta G^{o}_{ads}$  for the prepared surfactants indicate that the micellization and adsorption 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 theses molecules towards adsorption increase which result increase of the negativity values of  $\Delta G^{o}_{ads}$ . However, the high negativity values of  $\Delta G^{o}_{ads}$  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.

**Table 10**:Thermodynamic parameters of micellization of the synthesized ferrosurfactants.

Compound	Temp C°	ΔG° <sub>mic</sub> Kjmol <sup>-1</sup>	$\Delta S_{mic} = -\Delta G/T$ $Kjmol^{-1}_{k}$	ΔH <sub>mic</sub> Kjmol <sup>-1</sup>
	25	- 17.9995	0.1410	24.0396
III a	35	- 18.7873	0.1410	24.6619
	45	- 20.1968	0.1410	24.6624
	25	- 18.2048	0.1305	20.7038
III b	35	- 18.9456	0.1305	21.2679
	45	- 20.8149	0.1305	20.7036
	25	- 18.4018	0.1413	23.7268
III c	35	- 19.0739	0.1413	24.4676
	45	- 21.2283	0.1413	23.7263
	25	- 18.4588	0.1463	25.1605
III d	35	- 19.2439	0.1463	25.8383
	45	- 21.3848	0.1463	25.1605

**Table 11:** Thermodynamic parameters of adsorption of the synthesized ferrosurfactants.

Compound	Temp °C	ΔG° <sub>ads</sub> Kjmol <sup>-1</sup>	$\Delta S_{ads} = -\Delta G/T$ $Kjmol^{-1}_{k}$	ΔΗ <sub>ads</sub> Kjmol <sup>-1</sup>
	25	- 21.7287	0.1555	24.6336
III a	35	- 22.9039	0.1555	25.0134
	45	- 24.8379	0.1555	24.6344
	25	- 21.9064	0.1758	30.5084
III b	35	- 23.0023	0.1758	31.1705
	45	- 25.4220	0.1758	30.5087
	25	- 22.3761	0.1754	29.9194
III c	35	- 23.7437	0.1754	30.5758
	45	- 25.8841	0.1754	29.9194
	25	- 22.3685	0.1979	36.6354
III d	35	- 23.7564	0.1979	37.2265
	45	- 26.3266	0.1979	36.6352

#### 2.4. 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 <sup>[52]</sup>.

The selective permeability of the lipoprotein membrane represents the main function, namely controlling the 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<sup>[53]</sup>. Hence the positive charge of the cationic surfactant facilitates their interaction with the bacterial membrane, which lends them a good biocidal activity towards microorganisms <sup>[54, 55]</sup>.

The adsorptions at the water/cell membrane increase the hydrophobicity of that membrane which, increase its permeability towards 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 towards adsorption to wall of the tested microorganisms <sup>[56-57]</sup>.

 Table 12: Microbial inhibition zone of tested complexes in millimeters.

	Inhibition zone diameter of microorganisms in millimeters					
	<u>Bacillus</u>	<u>Escherichia</u>	<u>Candida</u>	<u>Aspergillas</u>		
Comp.	<u>sutilus</u>	<u>coli</u>	<u>albicans</u>	<u>nigar</u>		
	(G+ve)	(G -ve)	(Yeast)	(Mold)		
Control	0.0	0.0	0.0	0.0		
Water	0.0	0.0	0.0	0.0		
III a	24.5	22.5	24.6	23.3		
III b	19.5	20.0	16.0	13.2		
III c	19.0	15.0	12.0	12.0		
III d	13.0	13.5	11.0	11.3		

## IR spectra of compound before complexation:

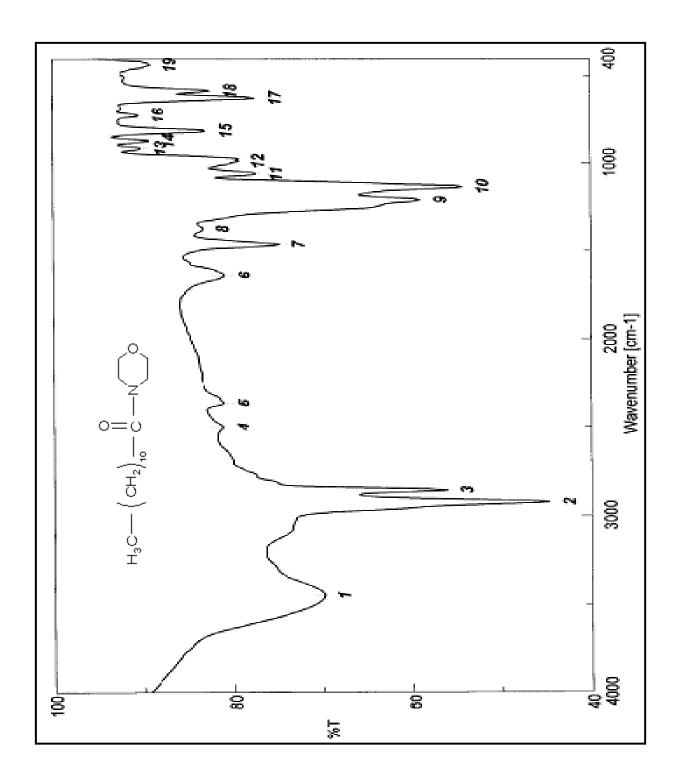


Fig. (14): IR Spectrum of morpholin -4-yl-dodecan-1-one (IIa)

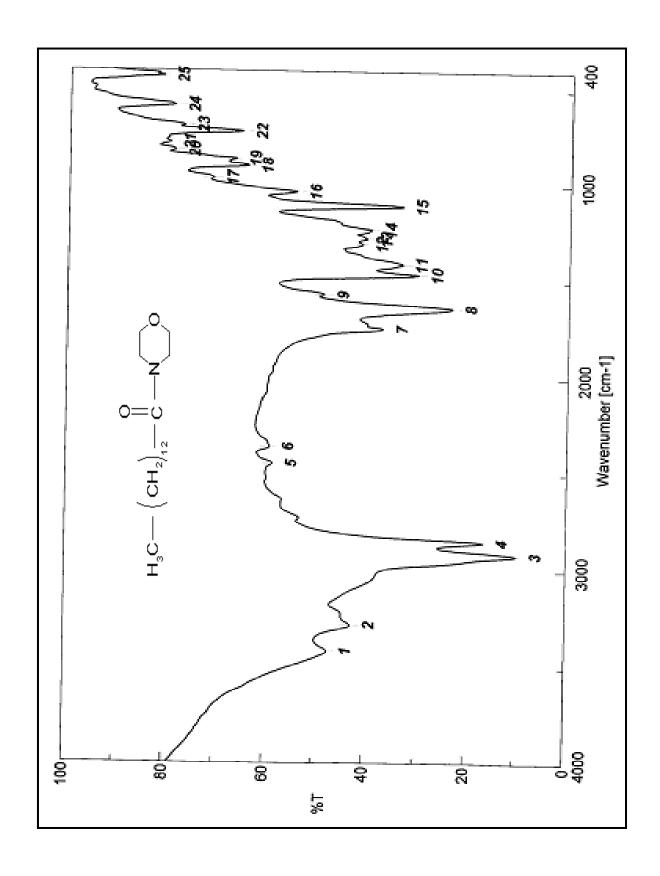


Fig. (15): IR Spectrum of morpholin -4-yl-tetradecan-1-one (II b)

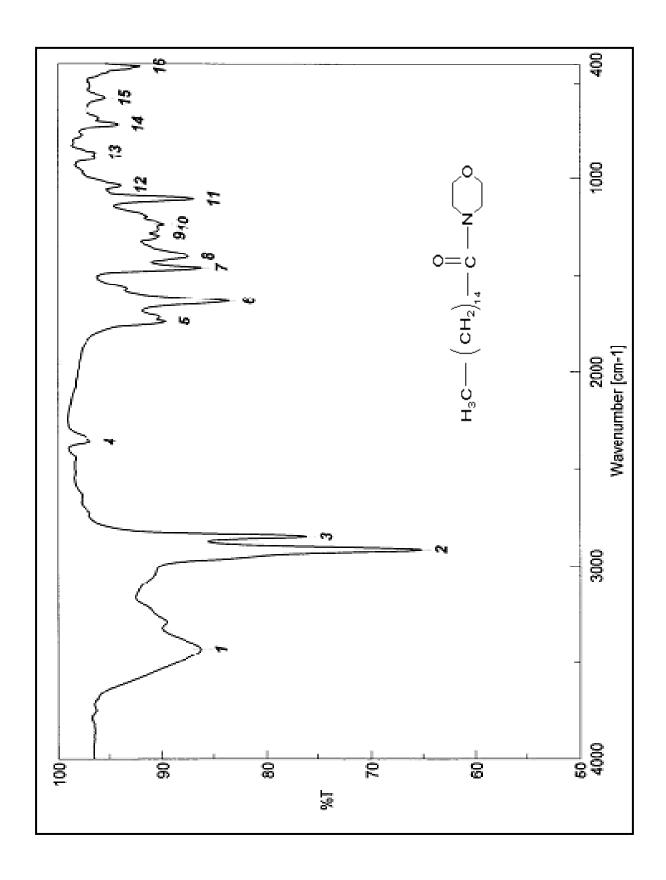


Fig. (16): IR Spectrum of morpholin -4-yl-hexadecan-1-one (IIc)

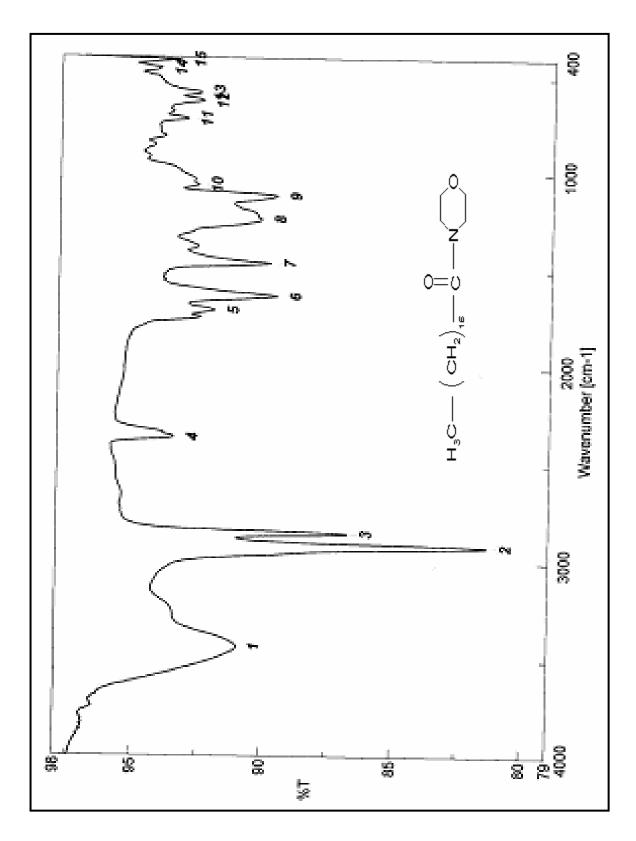
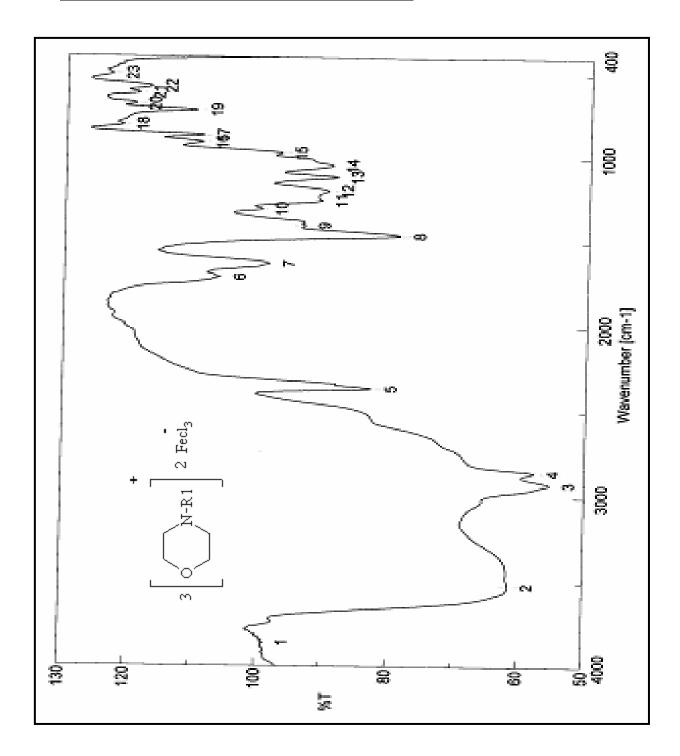
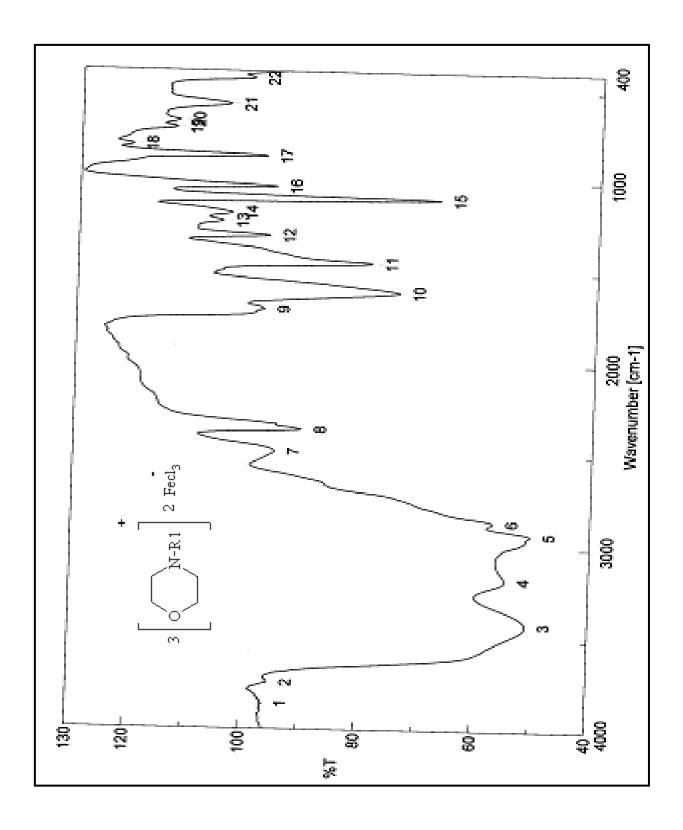


Fig.(17):IR Spectrum of morpholin -4-yl-octadecan-1-one (IId)

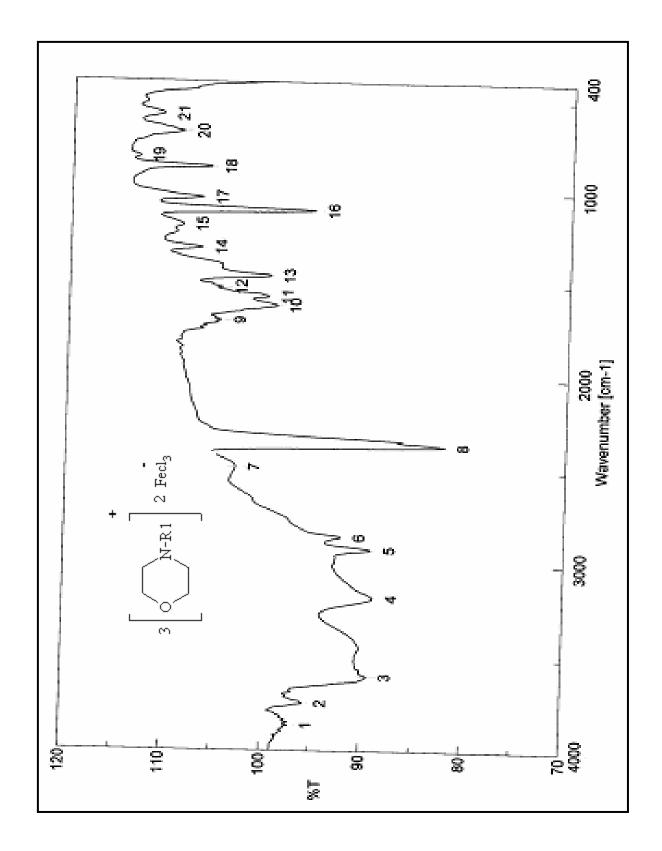
## IR spectra of compound after complexation:



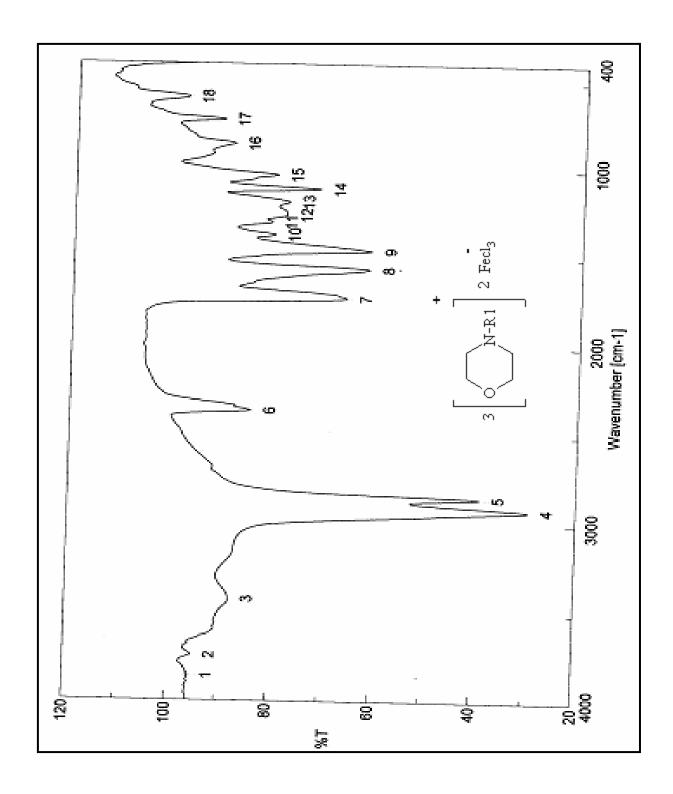
**Fig.** (18): IR spectrum of Tri [morpholin-4-yl-dodecan-1-one]-di [chloriumferriate] Complex (IIIa)



**Fig. (19):** IR spectrum of Tri [morpholin-4-yl-tetradecan-1-one]-di [chloriumferriate] Complex (IIIb).



**Fig. (20):** IR spectrum of Tri [morpholin-4-yl-hexadecan-1-one]-di [chloriumferriate] Complex (III c)



**Fig. (21):** IR spectrum of Tri [morpholin-4-yl-octadecan-1-one]-di [chloriumferriate] Complex (III d).

## <sup>1</sup>H-NMR spectra of compound before complexation:

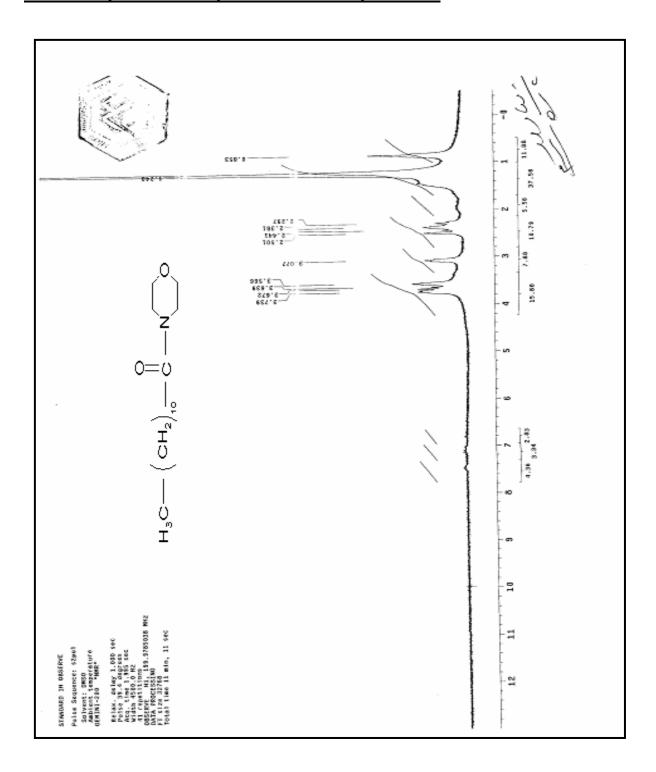


Fig. (22): <sup>1</sup>H-NMR Spectrum of morpholin -4-yl-dodecan-1-one (II a).

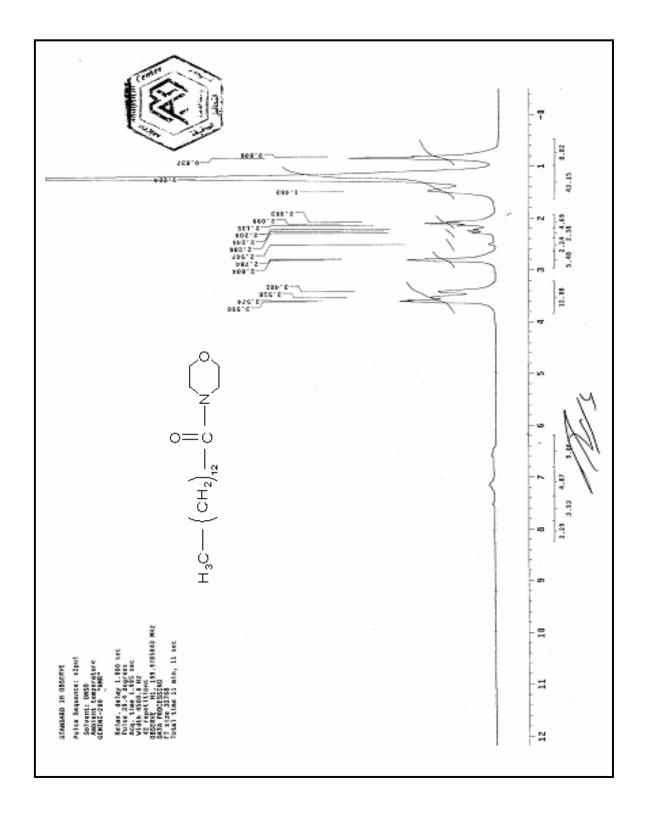
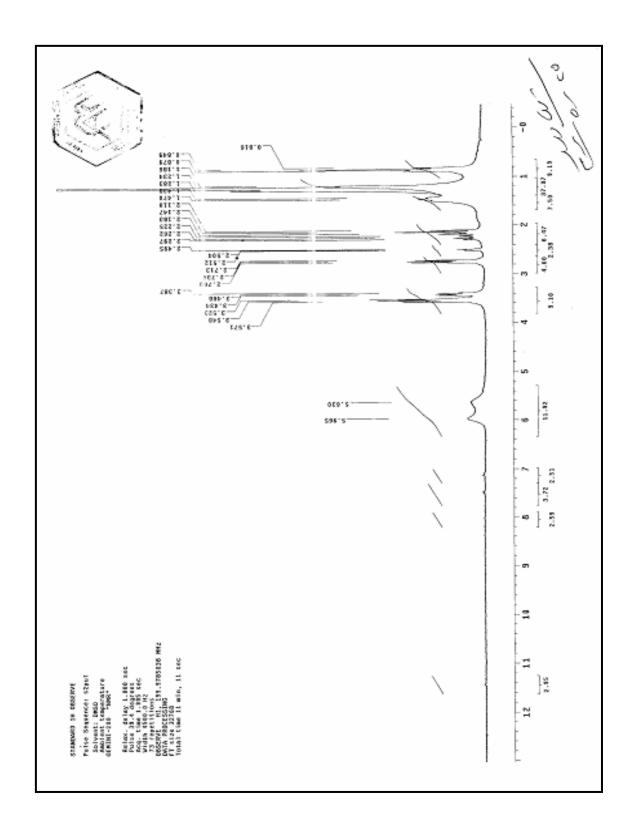


Fig. (23): H-NMR Spectrum of morpholin -4-yl-tetradecan-1-one (II b).



**Fig. (24):** <sup>1</sup>H-NMR Spectrum of morpholin -4-yl-hexadecan-1-one (IIc).

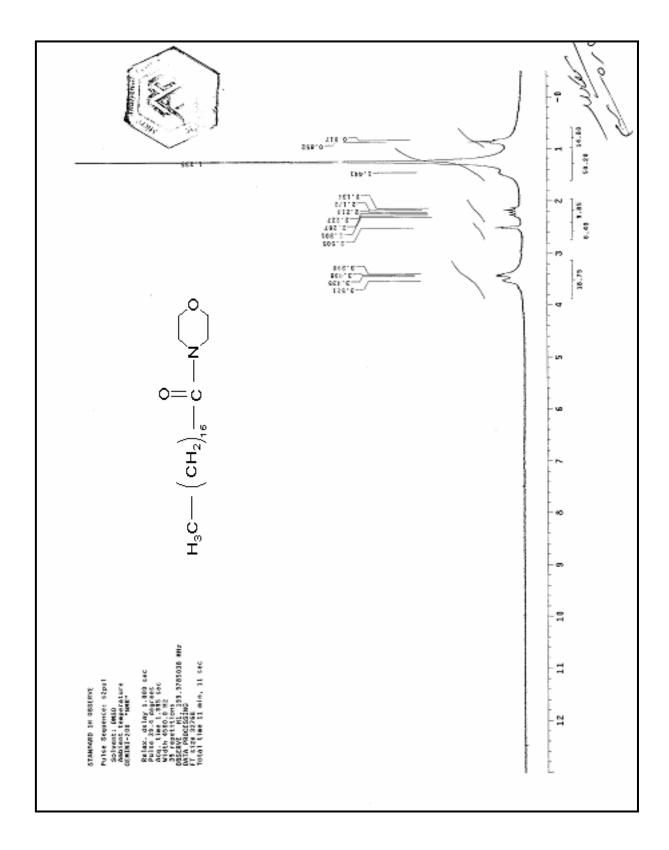


Fig. (25): <sup>1</sup>H-NMR Spectrum of morpholin -4-yl-octadecan-1-one (IId).