

## Synthesis, Characterization and Corrosion study of new Copolymers

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### الخلاصة

تم تحضير اثنين من البوليمرات المشتركة الجديدة وهما (Undecyl acrylate)(T<sub>1</sub>) و (Pentadecylacrylate)(T<sub>2</sub>) باستخدام (2-acrylamido-2-methylpropanesulfonic acid) وتم تشخيص على المركبات المحضرة بواسطة (FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, CHN) ثم دراستها كمثبطات تآكل لصلب الكربون في محلول (HCl)(1M) حيث تم قياس معدل التآكل بطريقة فقدان الوزن. وقد خلصت الدراسة على ان البوليمرات المشتركة تمنع عملية التآكل وبفعالية (93.3,97.3%) على التوالي في وقت (2 ساعة) ، وتركيز (1M) ودرجة حرارة 30 درجة مئوية.

### Abstract

Two new copolymers (T<sub>1</sub>, T<sub>2</sub>) were prepared, namely (Undecyl acrylate). (Pentadecyl acrylate). With (2-acrylamido-2-methylpropane sulfonic acid). (The prepared compounds were identified by (FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, CHN).The copolymers were study as corrosion inhibitors for carbon steel in (HCl) solution (1M) where the corrosion rate was measured by weight loss method. The weight loss measured indicate that the copolymers (T<sub>1</sub>, T<sub>2</sub>) were prevent and efficiently (93.3,97.3%) corrosion of inhibitors respectively at a time (2 h), concentration (1M) and a temperature of 30 °C.

**Keyword:**Synthesis ,Copolymer , CorrosionInhibitor

### 1.Introduction

A very unique chemical reaction occurs that allows chemical energy to be transferred into electrical energy, When two metals with different electronic potentials come into contact through a conductive medium in an electrolyte solution(1, 2). The behavior will eventually cause the physical properties of a metal to change and initiate the macroscopic signs of corrosion. The two centers where the reactions occur are termed as anode and cathode, of which the anode supplies electrons to the cathode. Among the several methods of corrosion control such as cathodic protection (3, 4), anodic protection (5), coating (6) and alloying, the use of chemical inhibitors is often considered as the most effective and practical method of corrosion prevention. A corrosion inhibitor is a chemical additive which when added to a corrosive

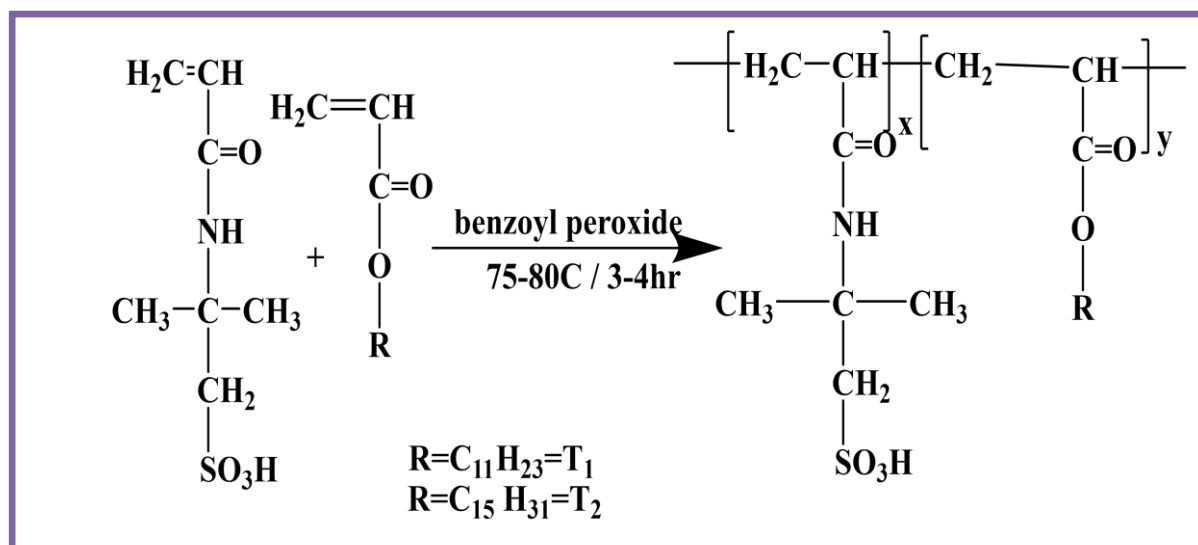
aqueous environment reduces the rate of metal wastage. The inhibitors especially that, the organic ones work by an adsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino ( $-\text{NH}_2$ ), carboxyl ( $-\text{COOH}$ ) and phosphate ( $-\text{PO}_3\text{H}_2$ ) although other functional groups or atoms can form by coordinate bonds with metal surfaces. Sanyal (7) and Abd El-Maksoud (8) in their reviews have given a vivid account of organic compounds used as corrosion inhibitors including their classification and mechanism of action. Raja and Sethuraman (9) has given a comprehensive review of natural products as corrosion inhibitors for metals in corrosive media. Natural products otherwise tagged "green were used as corrosion inhibitors" has been advocated because of the cost, toxic nature and environmentally unfriendliness of inorganic and organic corrosion inhibitors. They are readily available, cheap and a renewable source of materials. The use of polymers as corrosion inhibitors has attracted considerable attention recently. Polymers are used as corrosion inhibitors because, through their functional groups they form complexes with metal ions and on the metal surface these complexes occupy a large surface area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution (10). The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen) that are the major active centers of adsorption. The present work presents a review of copolymers as corrosion inhibitors, which completed to the previous our work for various metals in various aqueous corrosive environments. Investigated using weight loss measurements, galvanostatic polarisation studies, electro permeation studies and a.c. impedance measurements (11,12). The polymer acts predominantly as an anodic inhibitor. Hydrogen permeation studies and a.c. impedance measurements clearly indicate a very effective performance of the compound as a corrosion inhibitor. The adsorption of the compound on the mild steel surface obeys Tomkins's adsorption isotherm.

## **2. Materials and Methods**

### **2.1. Synthesis of Copolymers $T_1, T_2$**

The copolymers surfactant were prepared by mixing (2 g, 0.01 mol) 2-acrylamide-2-methylpropane sulfonic acid dissolved in (10ml) DMF with (3g, 0.01mol) Undecyl acrylate ( $T_1$ ) and (3.2g, 0.01mol) Pentadecyl acrylate ( $T_2$ ) in a (250ml) circular flask and the reaction was heated at a temperature of 75-80°C in the presence of nitrogen gas and a little benzoyl peroxide was added as a polymerization initiator with continuous stirring for (3-4 hrs), then the

product was left to cool and a mixture of diethyl ether was added for the purpose of washing, drying and disposal. Excess solvent. As in scheme (1).



Scheme(1).Synthesis of Copolymer

### 2.2.Wear velocity measurement

By taking rectangular pieces from the N-80 carbon steel models (with dimensions of (46cm, 3cm, 19cm) for each length, width and thickness, respectively, for the purpose of checking by weight loss measurement method, then the models were washed with dilute hydrochloric acid solution. The dimensions of the carbon steel model N-80 were measured by Venire to calculate the surface area of the model (length, width, thickness). Then , was weighed using the four decimal places sensitive scale. The model was immersed in the edible medium (1M hydrochloric acid) for two hours. And then it was cleaned. The model after extracting it from the medium, eating it with a piece of cotton, removing the erosion products. Weigh the model after cleaning and drying. Calculate the erosion velocity using equation (1). Then the experiment is repeated after adding the corrosion inhibitors in concentrations (0.01,0.02,0.03M) to the edible medium. And at different temperatures (40,50,60)<sup>0</sup>C and time (2hr).

$$R_{corr} = \frac{\Delta W}{St} \dots \dots \dots (1)$$

R<sub>corr</sub> = wear velocity gm.cm<sup>-2</sup>.hr<sup>-1</sup>

ΔW = weight loss gm

S = surface area cm<sup>2</sup>

t = time (hr).

### 3. Characterizations

#### 3.1.Infrared spectrum of the two copolymer inhibitors.

The infrared spectrum of the T<sub>1</sub> copolymer inhibitor was characterized by the presence of a wide band at the range (3444 cm<sup>-1</sup>) which represents the NH band - (amide. It appeared broadly because of the hydrogen gas. While a sharp band appeared for the group (C=O) ester at a range of (1728 cm<sup>-1</sup>) While a sharp band appeared for the group (C=O) Alameda at a range of (1658 cm<sup>-1</sup>). The CH<sub>2</sub> group bent bundle appeared at a range of 1469cm<sup>-1</sup>. A group beam (S=O) was distinguished at a range of -1 1388 cm. A bundle of group (S-O) appeared in a range of (1041 cm<sup>-1</sup>). The amplitude oscillation beams of a group (C-O) appeared at a range of (1118 cm<sup>-1</sup>). As for the signal at the site (3140 cm<sup>-1</sup>) it belongs to the (C-H) Alphabet group.as in the figure (1).

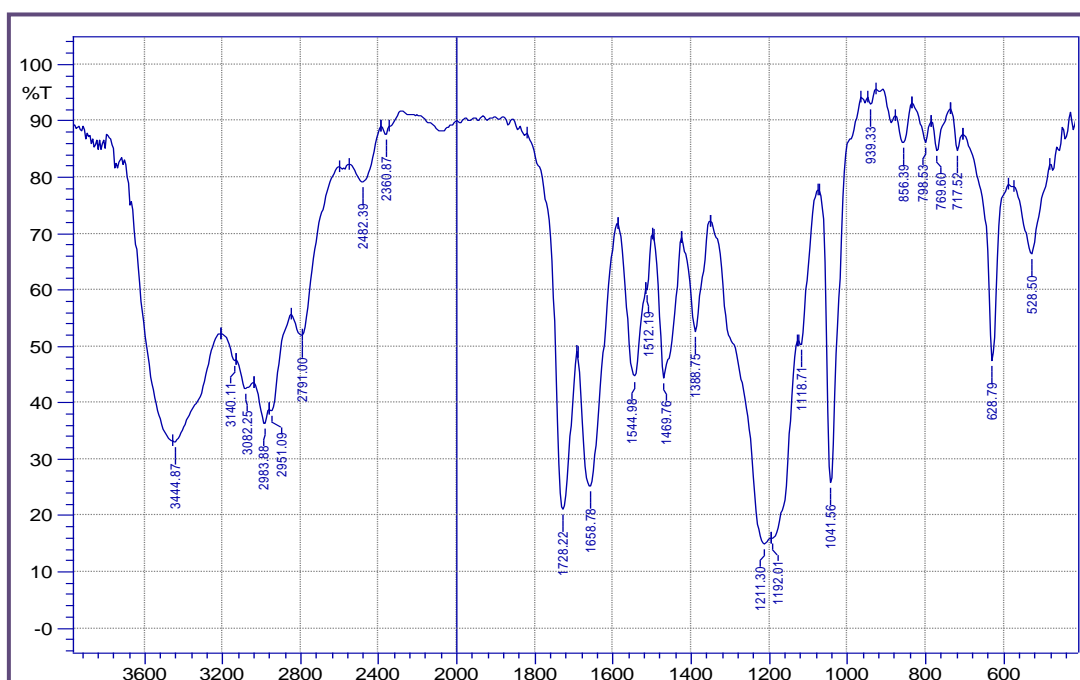
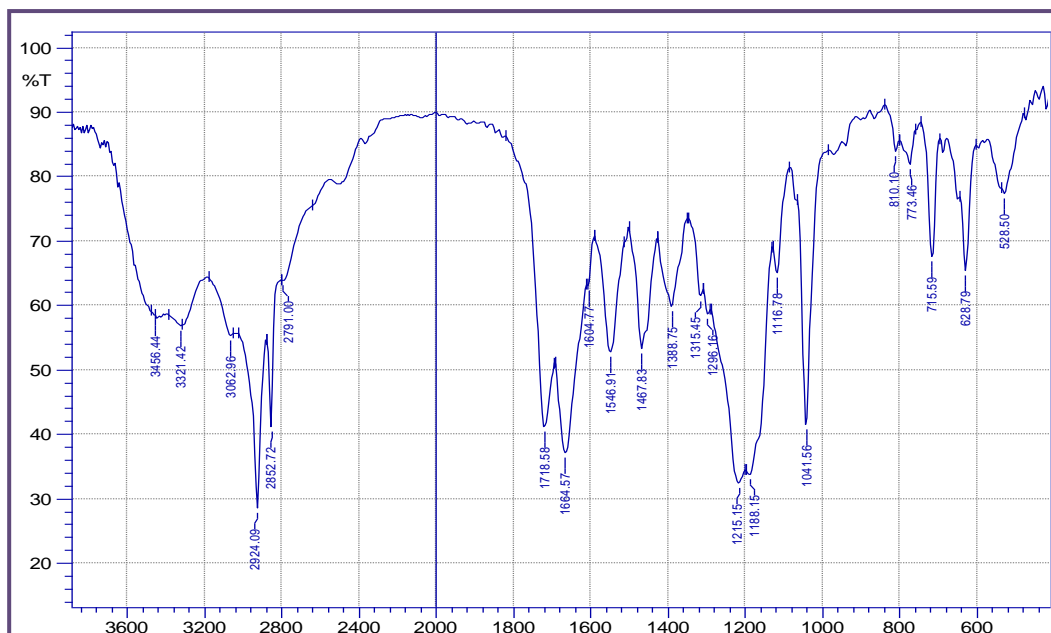


Figure (1) IR spectrum of the T<sub>1</sub> copolymer

### 3.2. Infrared spectrum of the T<sub>2</sub> copolymeric inhibitor.

The infrared spectrum of the T<sub>2</sub> copolymeric inhibitor was characterized by the presence of a wide band at the range (3456 cm<sup>-1</sup>) which represents the amide (NH) band. It appeared broadly because of the hydrogen gas. While a sharp band for the (C=O) ester group appeared at a range of (1718 cm<sup>-1</sup>). While a sharp band appeared for group (C=O) Alameda at a range of (1664cm<sup>-1</sup>). The CH<sub>2</sub>-group flexural package appeared at a range of (1467cm<sup>-1</sup>). A group beam (S=O) was distinguished at a range of (1388cm<sup>-1</sup>). A beam of a group (S-O) appeared in a range of (1041cm<sup>-1</sup>). The amplitude oscillation beams of a group (C-O) appeared at a range of (1116cm<sup>-1</sup>). As for the signal at the site (3321cm<sup>-1</sup>) it belongs to the (C-H) Alphabet group.as in the figure ( 2)



**Figure (2) IR spectrum of the T<sub>2</sub> copolymer**

### 3.3. <sup>1</sup>H-NMR spectrum of the T<sub>1</sub> copolymer

The figure (3) show that there is a signal at ppm (7.8ppm) that belongs to the proton of the sulfonic group, and a signal at the position (7.9ppm) that belongs to the proton of the (NH) group, and the signal that appears at the position (2.9ppm) belongs to the (CH<sub>2</sub>-) group linked With a sulfonic group, there is an indication at the 2.5ppm site that belongs to the two (CH-) groups present in the polymeric chain. As for the sign of the two groups (CH<sub>2</sub>-) of the polymeric chain appeared at the site (1.5ppm) while the group (CH<sub>3</sub>-) present in the compound appeared at the site (0.8ppm).

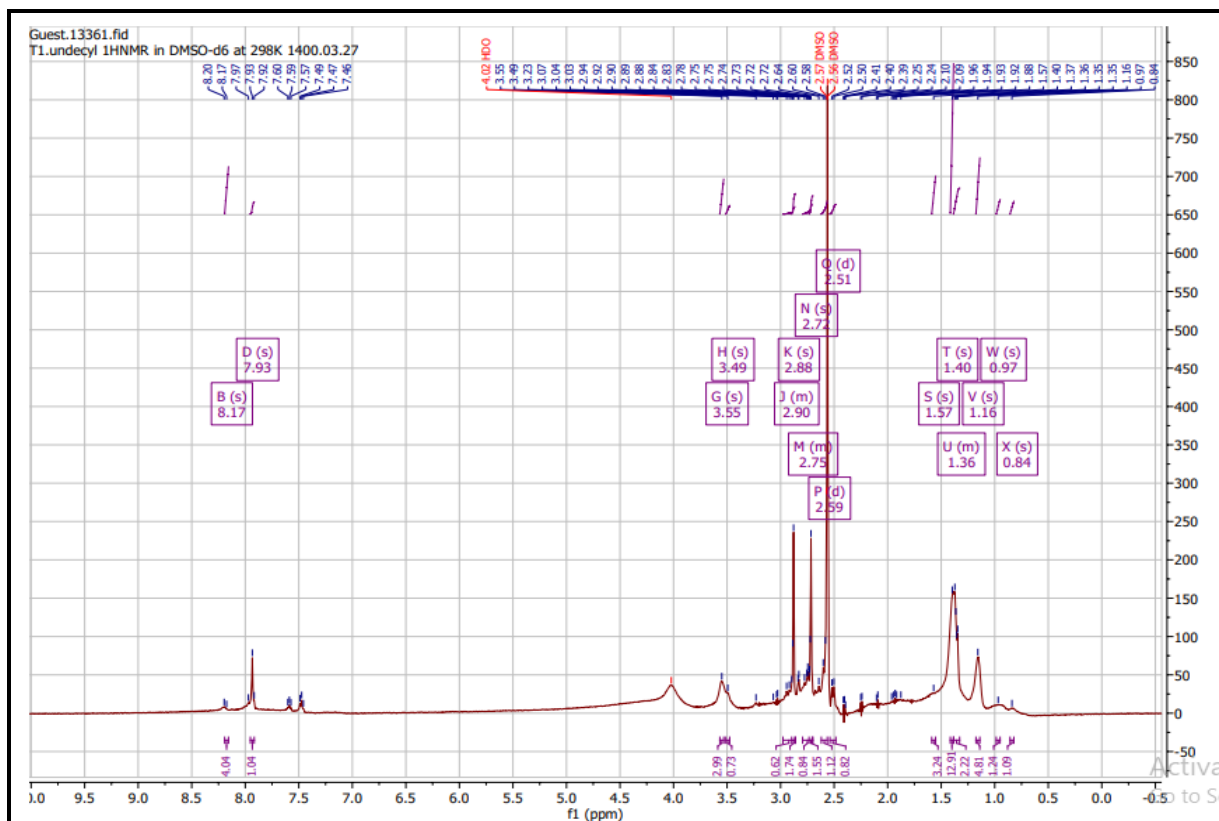


Figure (3)  $^1\text{H-NMR}$  spectrum of the  $\text{T}_1$  copolymer

### 3.4. $^1\text{H-NMR}$ spectrum of the $\text{T}_2$ copolymer

Figure 4 shows that the signal at ppm (7.8 ppm) belongs to the proton of the sulfonic group, the signal at position (7.3 ppm) belongs to the (NH) group proton, and the signal at position (2.2 ppm) belongs to The group ( $\text{CH}_2$ -) is associated with the sulfonic group, and the indicator is located at a position (2.8 ppm) belonging to the two groups ( $\text{CH}$ -) present in the polymeric chain. As for the sign of the two groups ( $\text{CH}_2$ -) of the polymeric chain, it appeared at the site (1.17 ppm), while the group ( $\text{CH}_3$ -) appeared in the compound at the site (1.04 ppm).

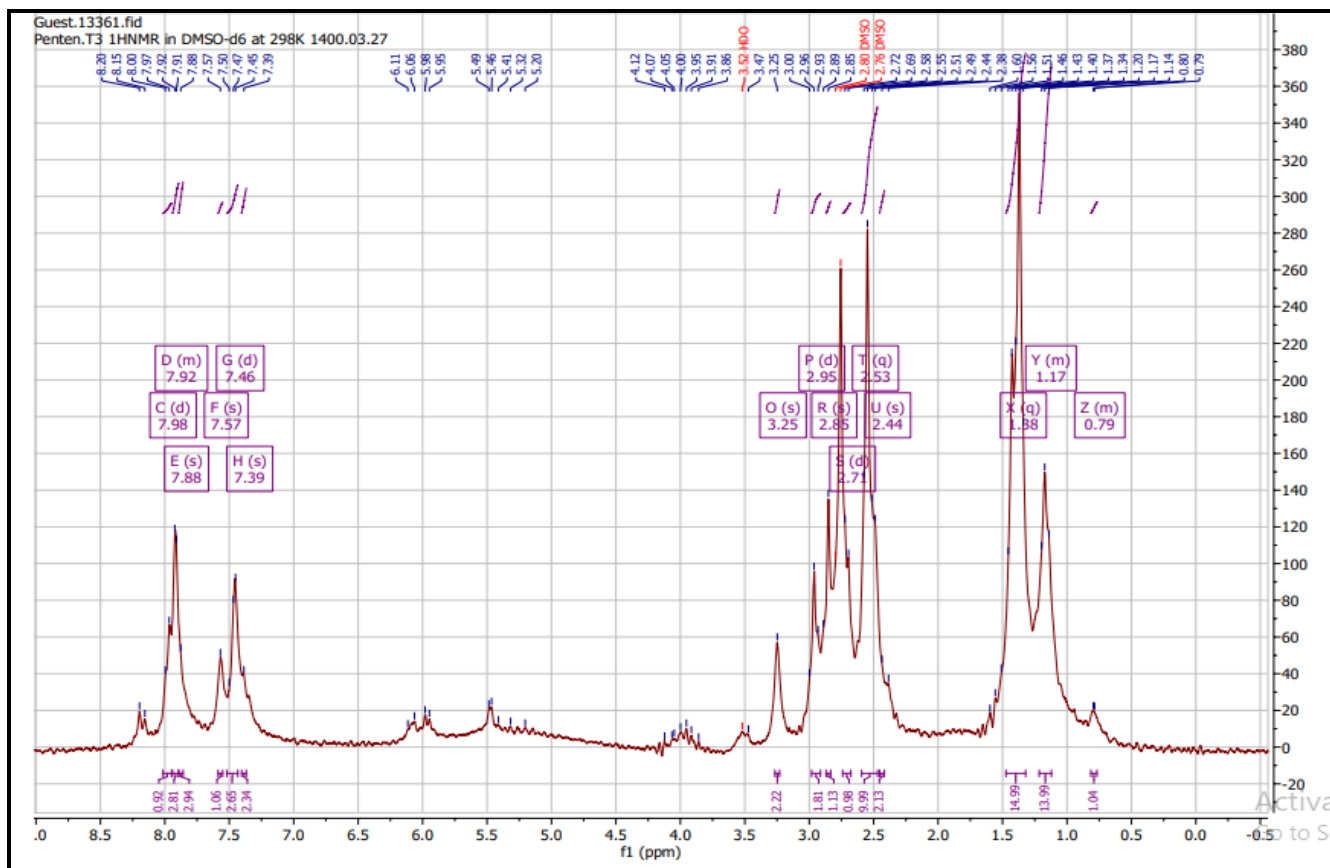


Figure (4)  $^1\text{H-NMR}$  spectrum of the T2 copolymer

### 3.5. $^{13}\text{C-NMR}$ spectrum of the $\text{T}_1$ copolymer

We notice from Figure (5) the appearance of a signal at the site (167ppm) belonging to the carbon atom in the ester carbonyl group. As for the amide carbonyl group, it appeared on the site (162ppm). There is a signal at (35ppm) belonging to the quaternary atom carrying the two groups of the same, while the signal at the position (34ppm) belongs to the carbon atom of the group ( $-\text{CH}_2$ ) within the polymeric chain as well as in the remaining butyl group. As for the signals within the range (25-35ppm), they belong to the carbon atom groups ( $-\text{CH}_3$ ) present in the compound.



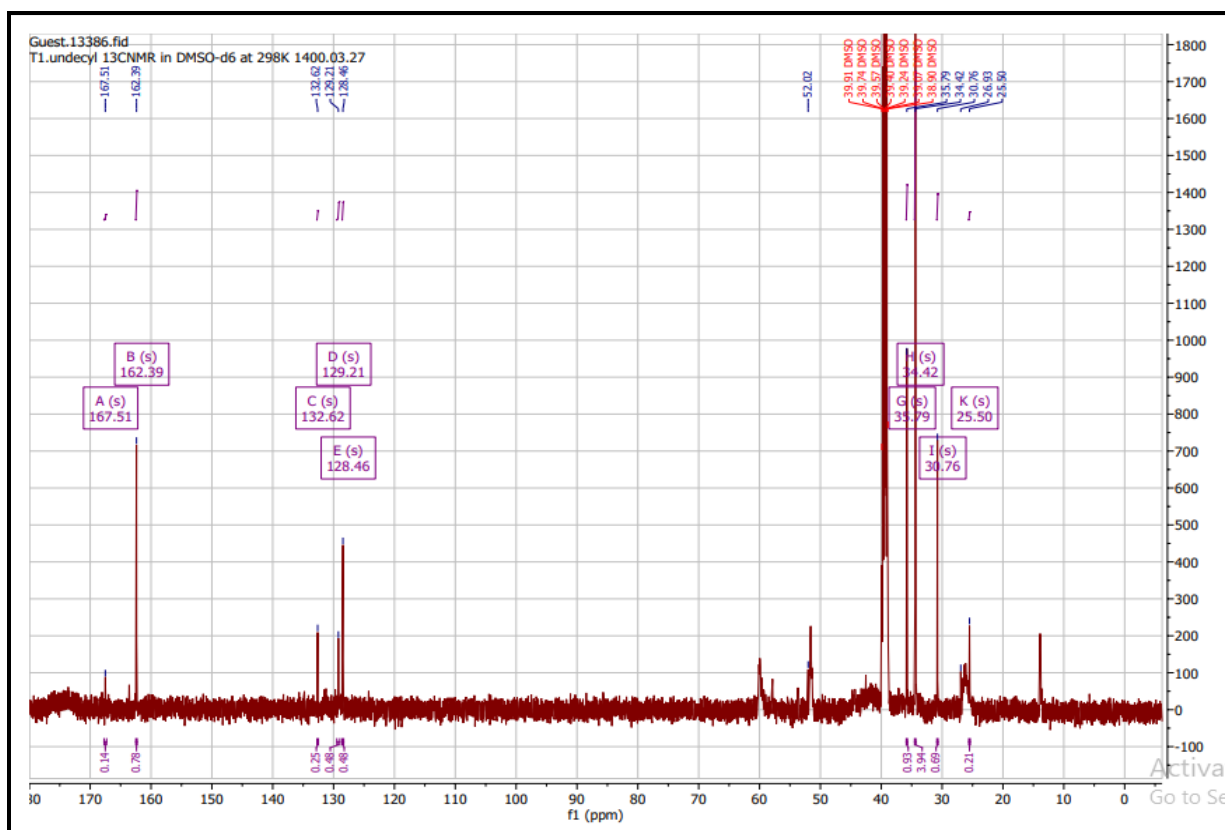


Figure (5)  $^{13}\text{C}$ -NMR spectrum of the  $\text{T}_1$  copolymer

### 3.6. $^{13}\text{C}$ -NMR spectrum of the $\text{T}_2$ copolymer

We notice from Figure (6) the appearance of a signal at the site (167ppm) belonging to the carbon atom in the ester carbonyl group. As for the amide carbonyl group, it appeared on the site (163ppm). There is a signal at (35ppm) belonging to the quaternary atom carrying the two groups of the same, while the signal at the position (34ppm) belongs to the carbon atom of the group ( $-\text{CH}_2$ ) within the polymeric chain as well as in the remaining butyl group. As for the signals within the range (10-20ppm), they belong to the carbon atom groups ( $-\text{CH}_3$ ) present in the compound.



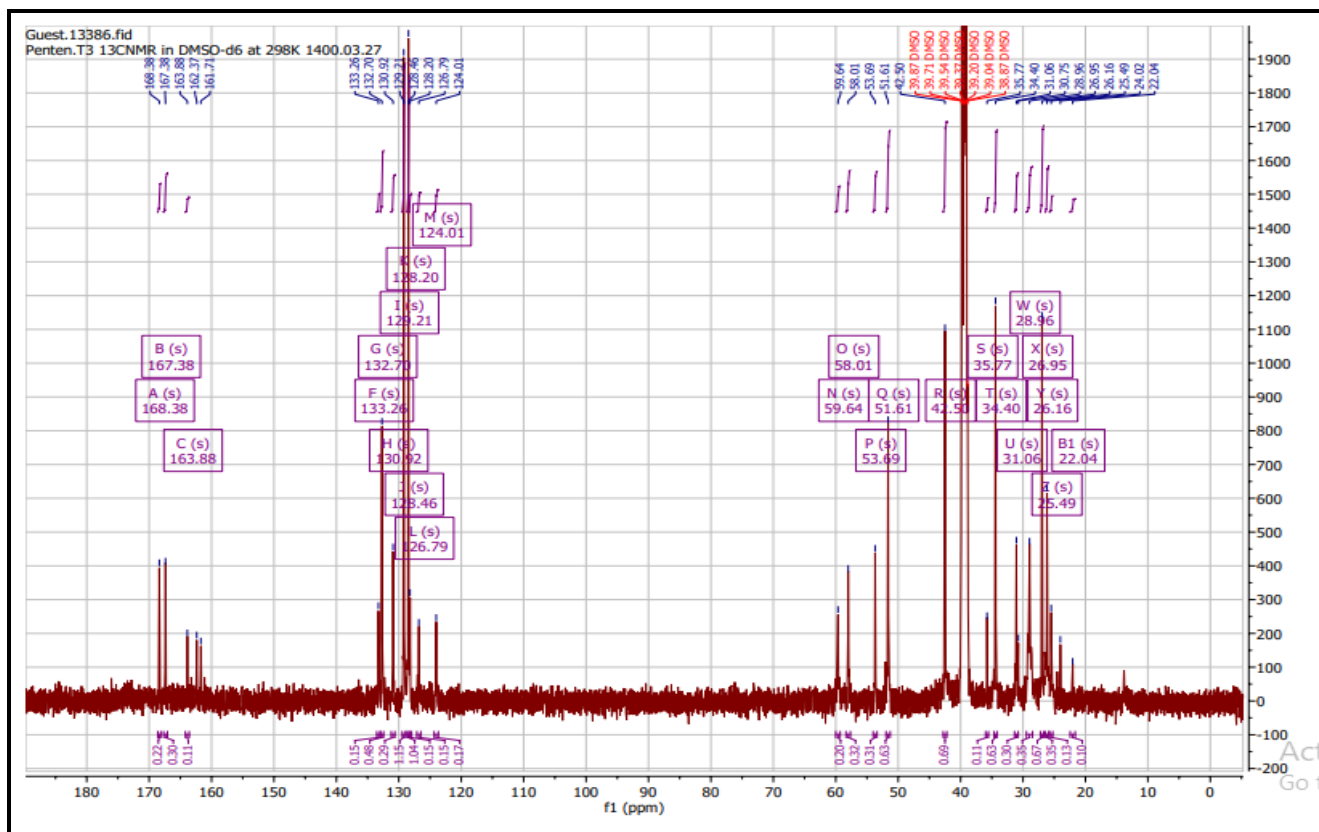


Figure ( 6) <sup>13</sup>C-NMR spectrum of the T<sub>2</sub>copolymer

#### 4. Results and discussions

##### 4.1. Estimate the proportions of the elements

The proportions of (C, H,N) elements were estimated for the prepared polymeric surfactants, and through them we could infer the validity of the prepared compositions if the calculated percentage of (C, H, N) was close to its calculated theoretical value as shown in the table (1 ).

**Table (1) Results of estimate in the proportions of trace elements C.H.N for the prepared compounds**

compound symbol	The molecular weight of the compound g/mol	Molecular formula	C%		H%		N%	
			theoretical	practical	theoretical	practical	theoretical	practical
T <sub>1</sub>	463.3	C <sub>23</sub> H <sub>45</sub> NO <sub>4</sub> S	59.5	59.93	9.70	9.78	1.50	1.65
T <sub>2</sub>	519.78	C <sub>27</sub> H <sub>53</sub> NO <sub>4</sub> S	362.2	62.39	10.19	10.25	1.34	1.30

##### 4.2. Study of erosion by weight loss method

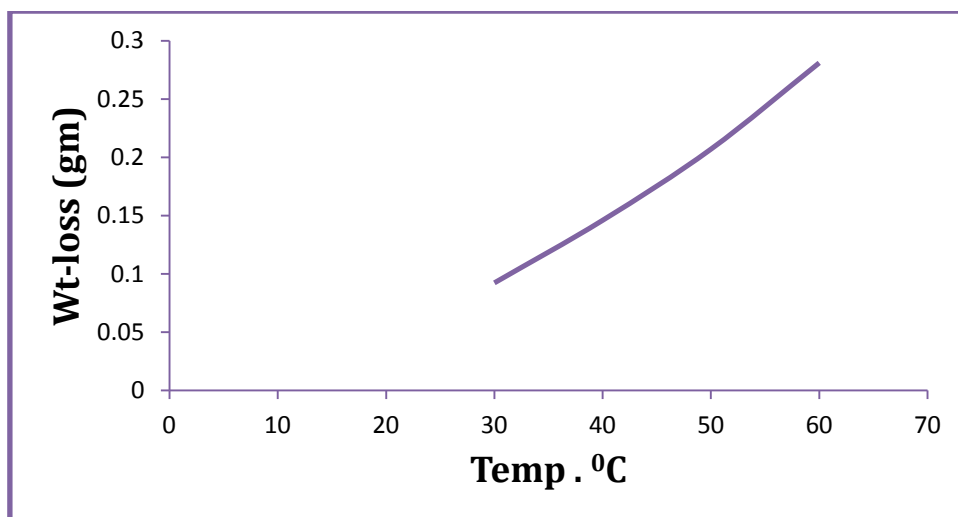
Study of the effect of temperature on the corrosion rate of carbon steel and weight loss in an aqueous solution of hydrochloric acid at a concentration of (1M) by a weight loss method with and without inhibitors.

Study of the corrosion rate of carbon steel in aqueous solution of acid (HCl) at a concentration of (1M) by weight loss method in the absence of inhibitors:

Measurement of the corrosion rate of carbon steel alloys of an aqueous solution of hydrochloric acid at a concentration of (1M) for two hours. and temperatures from 30-60°C. Through the results obtained, it was noted that the weight loss is directly proportional to the temperature to which the metal is exposed in the acidic solution. As in Figure (11) and Table (3). It was observed that the amount of weight loss increased from (0.0923) at a temperature of 30°C to (0.0146) at 40°C. But at a temperature of 50°C, the weight loss became (0.0207). Whereas at 60°C the weight loss was (0.0281) when the time (2hr) was set. While the average corrosion rate of carbon steel at a temperature of 30°C ( $11 \times 10^{-7}$ ) became. At 40°C it was ( $13 \times 10^{-7}$ ). While at 50°C ( $15 \times 10^{-7}$ ). at 60°C ( $17 \times 10^{-7}$ ).

**Table (3) Weight loss and corrosion velocity of carbon steel alloys in acidic medium (HCl) with a concentration of (1M) in the absence of an inhibitor**

Temp (C)	Wt-loss mg	R <sub>record</sub> gm.cm <sup>-2</sup> .hr <sup>-1</sup>
30	0.0923	11X10 <sup>-7</sup>
40	0.146	13X10 <sup>-7</sup>
50	0.207	15X10 <sup>-7</sup>
60	0.281	17X10 <sup>-7</sup>



**Figure (11) Weight loss and corrosion velocity of carbon steel alloy in acidic medium (HCl) with concentration (1M) as a function of temperature in the absence of inhibitor**

**Study of corrosion rate in an aqueous solution of acid (HCl) at a concentration of (1M) by weight loss method in the presence of inhibitors:**

The corrosion rate was studied in an aqueous solution of hydrochloric acid at a concentration of (1M) at a time (2hr) in the presence of inhibitors (A, B) at concentrations (0.01, 0.02, 0.03) as Tables (4) and (5). And figures (12) and (13). Weight loss results. Drift speed rate and R<sub>corr</sub>. The fraction of the metal surface covered with inhibitor particles (θ) and the inhibition efficiency (IE%). Which is obtained in the presence of inhibitors, where the percentage of inhibition efficiency was calculated through the following equation

$$\% \text{ IE} = 1 - (\text{Wadd}) / (\text{Wfree}) \times 100 \dots\dots\dots (2)$$

Wadd = Weight lost with damper (mg)

Wfree = Weight lost without damper (mg)

The part covered by the metal surface with inhibitor particles (θ) is calculated from the following equation:-

$$\theta = 1 - \text{Wadd} / \text{Wfree} \dots\dots\dots (3)$$

Study of the effect of temperature change on corrosion rate in an aqueous solution of hydrochloric acid at a concentration of (1M) by weight loss method in the presence of inhibitors Use different temperatures (30, 40, 50, 60) °C. The effect of these temperatures on the rate of corrosion speed and weight loss, as well as the percentage of retarding and the part covered with inhibitor molecules, was studied in the presence of different concentrations. (0.01, 0.02, 0.03M) in the presence of inhibitors (A, B). It is noted in Tables (4), (5).

Figures (12) to (15) show that the amount of weight loss with the presence of inhibitors is less compared to the absence of inhibitors. We also find that with increasing temperature, weight loss will increase with constant time (2hr). The results showed that the amount of weight loss increased from (0.923) at a temperature of 30°C to (0.281) at a temperature of 60°C in the absence of inhibitors. In the presence of inhibitors at a concentration (0.03 M) and at a constant time (2hr), the weight loss increased from (0.0402) at 30°C to (0.0706) at 60°C in the presence of inhibitor A. Inhibitor C, the amount of weight loss increased from (0.0184) at 30°C to (0.0709) at 60°C. As for the rate of velocity, it has been observed that the rate of corrosion of carbon steel with the presence of inhibitors is lower than in the absence of inhibitors. Corrosion rate of carbon steel in solution (HCl) (1M) at 30°C with time constant (2hr) and in the absence of inhibitor ( $11 \times 10^{-7}$ ) while inhibitors are present to ( $5 \times 10^{-7}$ ,  $2.33 \times 10^{-7}$ ) respectively at a concentration of (0.03M). While at 40°C in the absence of the inhibitor and at a constant temperature (2hr) the corrosion rate was ( $13 \times 10^{-7}$ ). While in the presence of dampers (A, B) to ( $4 \times 10^{-7}$ ,  $3.68 \times 10^{-7}$ ) at a concentration (0.03M) but at 50°C in the absence of damper and at constant temperature (2hr) the wear rate was ( $15 \times 10^{-7}$ ) While in the presence of inhibitors (A, B) to ( $2.08 \times 10^{-7}$ ,  $4.67 \times 10^{-7}$ ) respectively at a concentration of (0.03 M) but at 60°C in the absence of the inhibitor and when the temperature is constant (2hr) the corrosion rate was ( $17 \times 10^{-7}$ ) while in the presence of inhibitors (A, B) to ( $4.49 \times 10^{-7}$ ,  $4.50 \times 10^{-7}$ ) respectively at concentration (0.03 M) As for inhibitor A, it decreased from 93.3% at 30°C to 88.3% at 60°C. As for inhibitor C, the inhibition efficiency decreased from 97.3% at 30°C to 89.8% at 60°C.

**Table (4 ) represents the weight loss, the rate of corrosion speed, the part covered by the metal surface with inhibitor particles, and the percentage of inhibition for carbon steel alloy N-80 in HCl solution at a concentration of (1M) at different temperatures and time (2hr) in the presence of inhibitor A**

**Table (5) represents the weight loss, the rate of corrosion speed, the part covered by the metal surface with inhibitor particles, and the percentage of inhibition for carbon steel alloy N-80 in HCl solution at a concentration of (1M) at different temperatures and time (2hr) in the**

Time	30				40				50				60				
	Conc. (M)	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ
0.00	0.0923	$11 \times 10^{-7}$			0.146	$13 \times 10^{-7}$			0.207	$15 \times 10^{-7}$			0.281	$17 \times 10^{-7}$			
0.01	0.0242	$3.07 \times 10^{-7}$	87.9	0.879	0.0165	$1.57 \times 10^{-7}$	91.7	0.917	0.0553	$4.21 \times 10^{-7}$	72.4	0.724	0.0885	$5.62 \times 10^{-7}$	55.7	0.557	
0.02	0.0501	$6.36 \times 10^{-7}$	89.9	0.899	0.0388	$3.69 \times 10^{-7}$	92.2	0.922	0.0793	$6.04 \times 10^{-7}$	84.2	0.842	0.0918	$5.83 \times 10^{-7}$	81.6	0.816	
0.03	0.0184	$2.33 \times 10^{-7}$	97.3	0.973	0.0386	$3.68 \times 10^{-7}$	94.4	0.944	0.0613	$4.67 \times 10^{-7}$	91.2	0.912	0.0709	$4.50 \times 10^{-7}$	89.8	0.898	

**presence of inhibitor B**

Time	30				40				50				60			
Conc. (M)	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ	wt-loss gm	Record gm.cm <sup>-2</sup> .hr <sup>-1</sup>	% IE	Θ
0.00	0.0923	11X10 <sup>-7</sup>			0.146	13X10 <sup>-7</sup>			0.207	15X10 <sup>-7</sup>			0.281	17X10 <sup>-7</sup>		
0.01	0.0287	3.64X10 <sup>-7</sup>	85.6	0.856	0.0328	3.12X10 <sup>-7</sup>	83.6	0.836	0.0371	2.82X10 <sup>-7</sup>	90.7	0.907	0.0933	5.93X10 <sup>-7</sup>	53.5	0.535
0.02	0.0425	5.40X10 <sup>-7</sup>	89.3	0.893	0.0376	3.58X10 <sup>-7</sup>	90.6	0.906	0.0429	3.27X10 <sup>-7</sup>	78.6	0.786	0.0511	3.24X10 <sup>-7</sup>	87.3	0.873
0.03	0.0402	5X10 <sup>-7</sup>	93.3	0.933	0.0422	4X10 <sup>-7</sup>	92.9	0.929	0.0273	2.08X10 <sup>-7</sup>	54.5	0.545	0.0706	4.49X10 <sup>-7</sup>	88.3	0.883

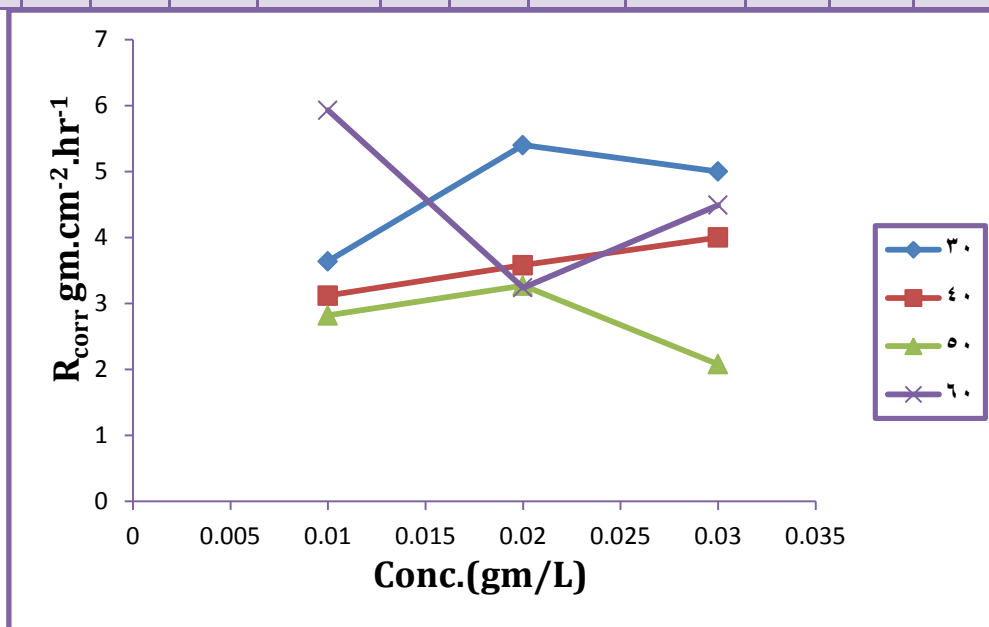


Figure (12) Average wear rate of carbon steel as a function of concentration in the presence of inhibitor A

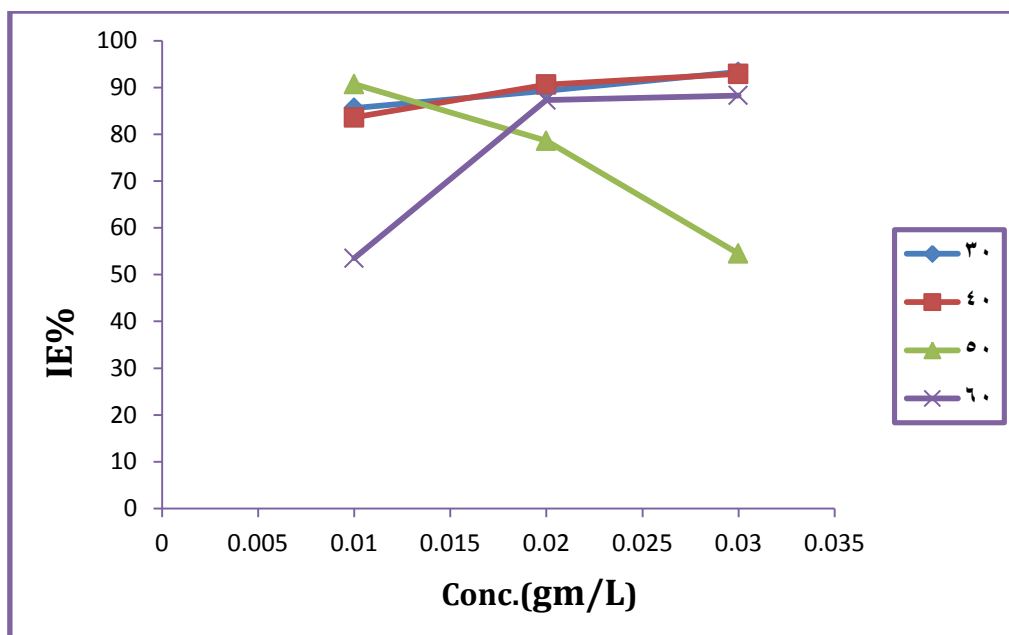


Figure ( 13 ) percentage of inhibition efficiency as a function of concentration in the presence of inhibitor A

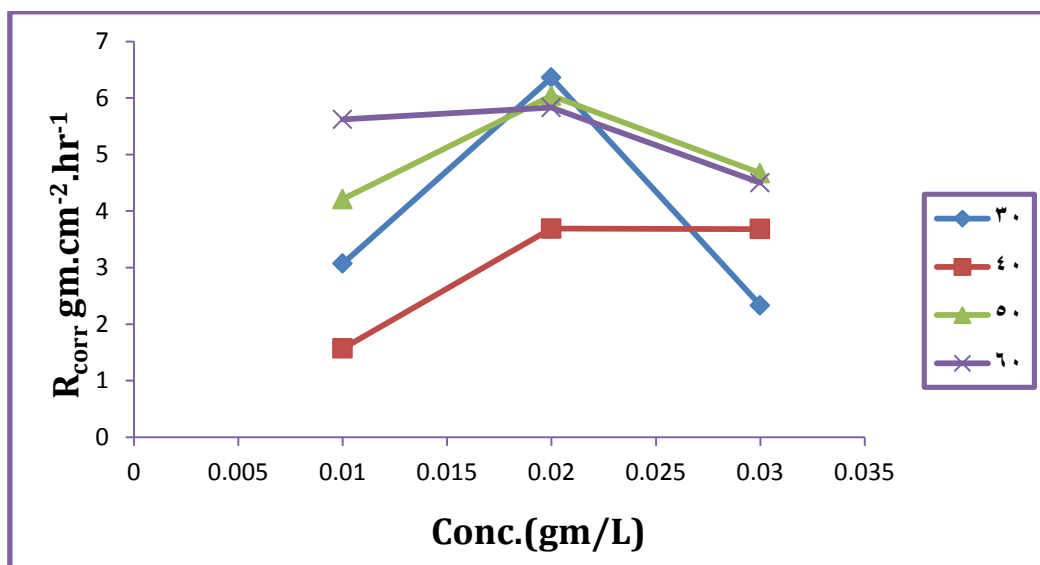
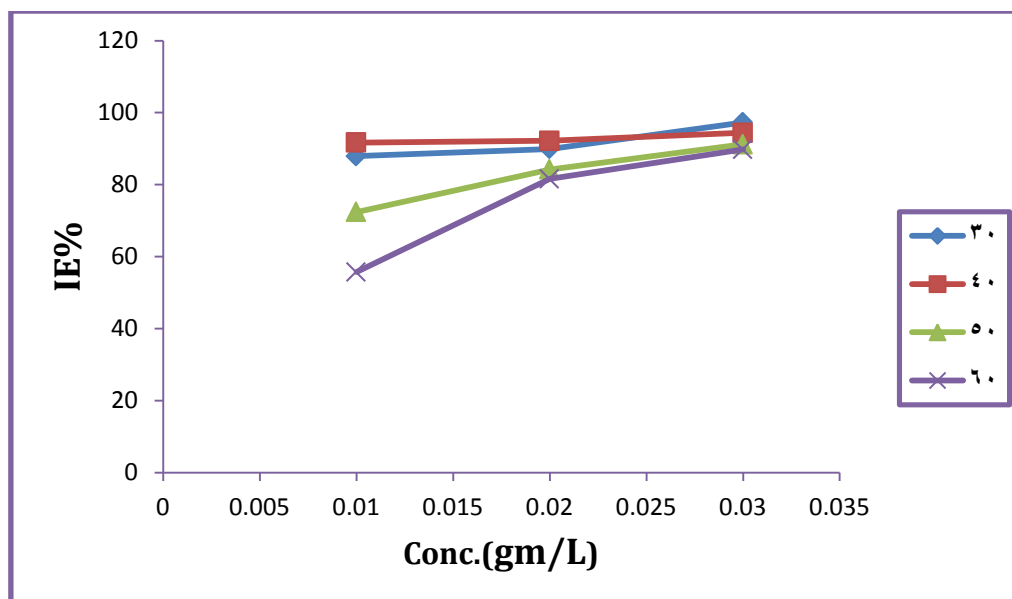


Figure (14) Average wear rate of carbon steel as a function of concentration in the presence of inhibitor B



**Figure ( 15) percentage of inhibition efficiency as a function of concentration in the presence of inhibitor B**

### Conclusions

It has been shown that the two copolymers are efficient corrosion inhibitors in different aqueous media. Mechanism of inhibition are mainly attributed to adsorption and depends on the metal, physicochemical properties of the molecule such as functional groups, steric factors, aromaticity at the donor atom and orbital character of donating electrons as well as the electronic structure of the molecules. The weight loss measured indicate that the copolymers ( $T_1$ ,  $T_2$ ) were act a good prevent and efficiently for corrosion as inhibitors.

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