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## **A Study of poly4-oxo-4-(4-sulfamoylphenylamino) but-2-enoic acid as a good anti – Corrosion of 316L stainless steel in 0.2M hydrochloric acid solution.**

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### **1. Abstract**

Poly4-oxo-4-(4-sulfamoylphenylamino) but-2-enoic acid (POSPAEA) was prepared by the electrochemical polymerization of 4-oxo-4-(4-sulfamoylphenylamino) but-2-enoic acid (OSPAEA) monomer on 316L stainless steel as anti-corrosion coating. scanning electron microscope (SEM) , Atomic Force Microscope (AFM) and Fourier transform infrared techniques (FTIR) were used to identify the structure of the polymer layer. also The corrosion behavior of uncoated and coated 316L stainless steel were estimated from Tafels plots using Potentiostatic technique in 0.2 M HCl solution as corrosion medium at temperature ranging ( 293 – 323) K. Nano materials such as graphene and ZnO Nano in different concentrations were added to monomer solution to improve the corrosion resistance of 316L stainless steel surface so that the results showed that the values of corrosion protection efficiency for coating polymer increase with adding Nano materials . In addition the kinetics and thermodynamics of parameter were calculated for corrosion process 316L stainless steel before and after polymer coating in the acidic medium.

**Keyword:** corrosion, electro polymerization, stainless steel, coating, sulfanilamide

### **2. Introduction**

The stainless steel type 316L (316LSS) is used extensively in numerous fields such as industrial and biomedical applications [1] due to its ability to form a protection oxide layer , which represses natural degradation processes and increase the corrosion resistance of SS316L in aqueous media[2] . but when the presence of this oxide layer in chloride containing environments such as HCl these (passive)oxide layers suffer from break down leading to the initiation and propagation of localized attack is known as pitting corrosion .[3]

Several attempts have been used to control the SS316L from undergoing corrosion in aggressive environments.[4] One of the interesting methods using conducting polymers[5-7], These polymers owing electrically conductive due to their widely  $\pi$ -conjugated backbone[8] that allow flow in the current at the metal of surface to suppress the corrosion reactions by their reversible redox activity.[9-19] They have been attracted most attention as advanced materials because of their higher



environmental stability, easy synthesis, cheapness, and their profound conduction mechanism[20-21]

Intrinsically conducting polymers polypyrrole, polythiophene, polyaniline and their derivatives have a big degree of applications,[22] such as antistatic film,[23] lithium batteries[24], sensors [25]and display corrosion protection of metal surface[26-27]. Using conducting polymers to protect metal against corrosion have been an investigation in several studies [28-33].

A number of different mechanisms for corrosion protection including conductive polymers were proposed [34], corrosion inhibitors, anodic and cathodic protection, and barrier protection. Anodic protection involves the formation of stable passive oxide film on the surface of the metal which can change the electrode potential in the passive side that prevents dissolution the metal and oxidize the monomers into polymers by using electro chemical polymerization process. This process is useful for synthesis of the polymer coating on the surface of stainless steel without any oxidant impurities [35].

Development of protective conductive polymers Nano materials coating on the metals and alloys is one of the interesting researches in corrosion protection of steel structures [36-37]. They are display enhanced electrical, mechanical, magnetic,opticals, and their corrosion resistant properties which are much better compared to their individual ingredients due to their electro active and conductivity nature of these polymer[38] . The conducting polymers Nano materials are the best candidates to reduce the rate of corrosion on steel structures [39]. The present study including characterize the structure of the prepared polymer film (OSPAEA) by using analysis (SEM, AFM, FT-IR) then study the corrosion behavior of uncoated and coated (316L) stainless steel with and without nano materials by using Potentiostatic technique in 0.2M HCl solution at different temperatures and calculated the kinetics and thermodynamics parameter for corrosion process .

### 3. Experimental

The electrochemical polymerization of (OSPAEA) on the 316L Stainless steel (anode) electrode surface was accomplished in a potentiostat using a regulated (DC) power supply. The electrodes were cleaned and washed by distilled water then acetone. The solutions employed for polymerization were 0.1g of (OSPAEA)) [40] in 100 ml of distilled water with three drops of H<sub>2</sub>SO<sub>4</sub> concentration (37%) as supporting electrolyte. The polymer film was deposited at the anodic surface. For corrosion measurements three-electrodes for cell including a working electrode (the Stainless-steel include coated and non-coated), reference electrode (SCE) and counter or auxiliary electrode (platinum electrode). Anodic and cathodic polarization of (316L) stainless steel was carried out under potentiostatic conditions in 0.2M HCl in the absence then in the presence-coated layer at different temperature from 293 to 323K.

Also in the presence 0.04g of Zn Nano material was added with the monomer solution and 0.004g of Graphene was dispersed by 1ml from H<sub>2</sub>SO<sub>4</sub> (37%) then was added with monomer solution to improve the coated layer against corrosion .

## 4. Result and discussion

### 4.1. Mechanism of polymerization

Depending on the published literature, Cationic [41-42] or radical mechanism [43-50] can be suggested to be expounding the electric polymerization reactions, in particular grafting and growth of the (POSPAEA) films. The first consider that is the cationic mechanism (fig1-A). Application of the anodic potential to (OSPAEA) solution reveals to the transfer of one electron from the monomer (OSPAEA) to the working electrode A1. This transfer for electron leading to formation radical cation adsorbed on the electrode surface which is appeared in (A2). alternatively, if the life time of (A2) is long enough compared to the middle time of the (OSPAEA) molecule to diffuse towards the electrode. Then the (OSPAEA) molecules can be added by the cationic mechanism at the charged end of oxidized (OSPAEA) name (A4). This process by the diffusion leading to formation the grafted polymer, now the second consideration is a radical mechanism [51]. The radical counterpart of (A) is (B).first; the chemisorbed radical depicted in (B2) cannot be the result of the electro chemical process. If we suppose that the grafting step is disconnected from electro chemical process. We faced the fact that the radical mechanism is not specially favored through the current electro chemical conditions .actually , the radical mechanism proceed carry on through the hemolytic fusion of the double bond (Fig1-B) however ,the dissolution of the ( C=C ) is very unlikely given the initial polarization of the bond ,which is further promoted under the field generated by the electric double layer [52].the reorientation of the molecule has been catalyzed by this electric field[52]. This all jointly makes the radical mechanism improbable to represent the growth of (POSPAEA) film under the anode electrochemical condition.

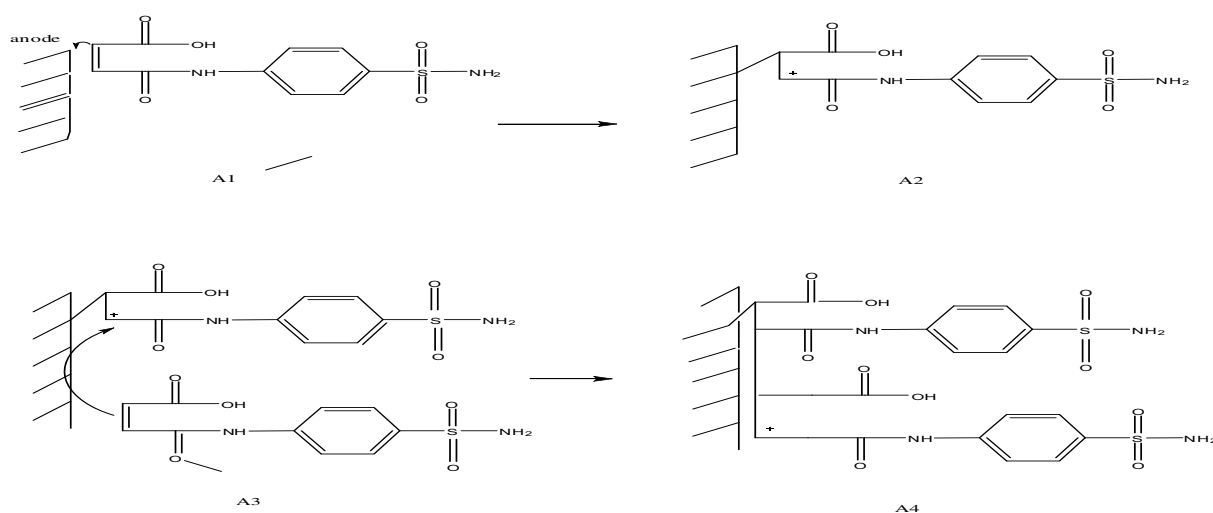


Figure (1-A): Cationic mechanism for the Grafting and the Growth of POSPAEA Films.

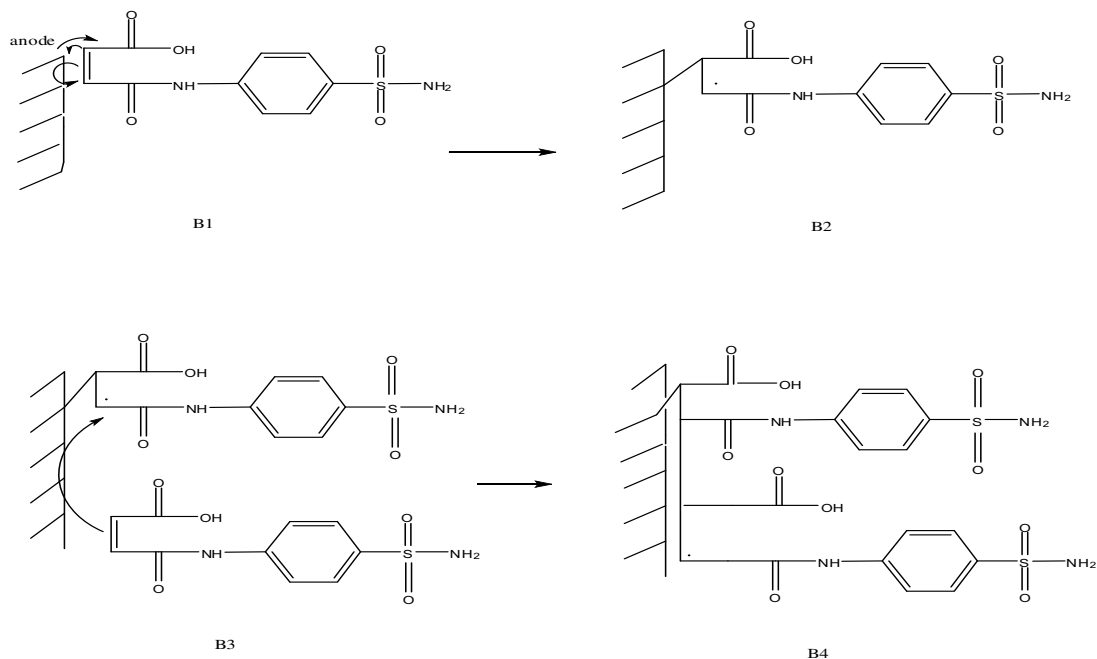


Figure (1-B): Free radical mechanism for the Grafting and the Growth of POSPAEA Films.

## 4.2. The structure of POSPAEA

### 4.2.1. FT-IR analysis

The coated film of polymer (POSPAEA) Fig (3) is prepared from the monomer (OSPAEA) and examined by FT-IR spectroscopy. The absorption bands of the (OSPAEA) Fig 2 shows  $\text{HC}=\text{CH}$  olefinic group appeared at  $3107\text{ cm}^{-1}$ , the band of  $\text{C}=\text{O}$  carboxyl group appeared at  $1699\text{ cm}^{-1}$ , the absorption of  $-\text{NH}_2$  amine group represented at  $3261\text{ cm}^{-1}$  symmetric and asymmetric at  $3350\text{ cm}^{-1}$ , the peaks at  $3210\text{ cm}^{-1}$  attributed to the amide group. In Figure (3) we noticed disappeared the double bond  $\text{C}=\text{C}$  olefinic group that confirm the formation of POSPAEA. The bands comparatively broad because the polymer POSPAEA has abroad chain extent distribution [54-56]

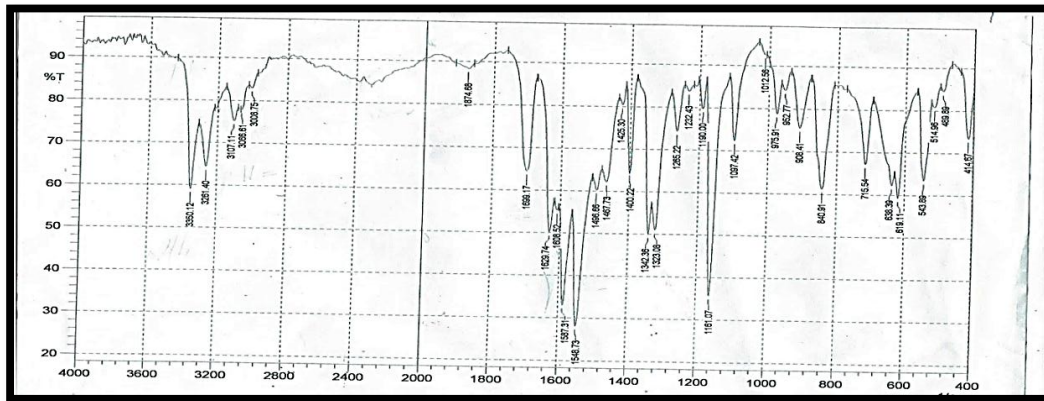


Figure (2): FTIR for OSPAEA

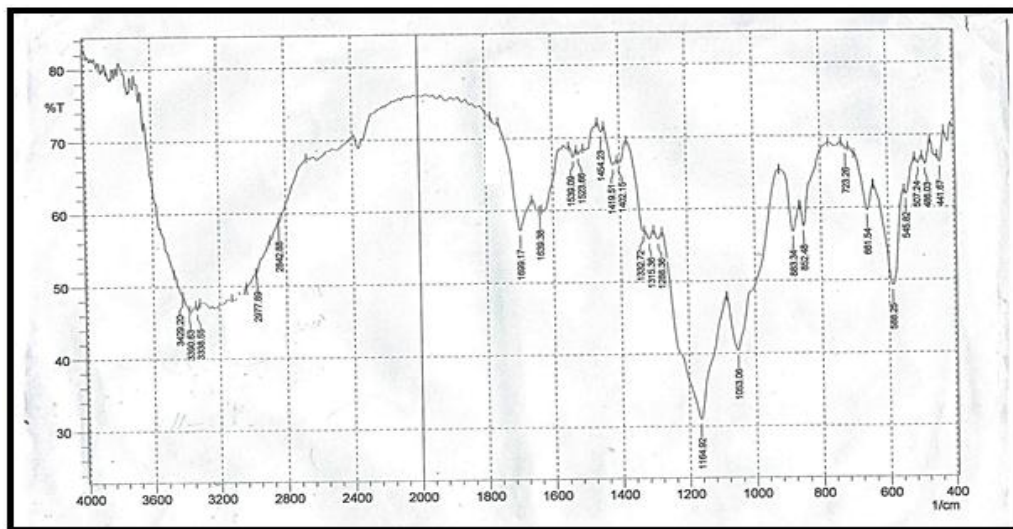


Figure (3):FTIR for POSPAEA

#### 4.2.2. Atomic force microscope (AFM)

The surface topography of the stainless steel coated with POSPAEA in absence and presence of Nano materials [graphene and ZnO (Nano)] was investigated through AFM technique. (Fig4) show the 3D of the AFM images of all applied coated films. In AFM analysis, the diameter average, roughness average ( $R_a$ ) and Root Mean Square (RMS) are the most used parameters to characterize the surface roughness. These parameters are represented in table (1) the results indicate there is decrease in the surface roughness for three coated films with decrease in the diameter Average and the lower roughness surfaces act a good barrier favorably effect for protection the coatings from corrosion.[57]

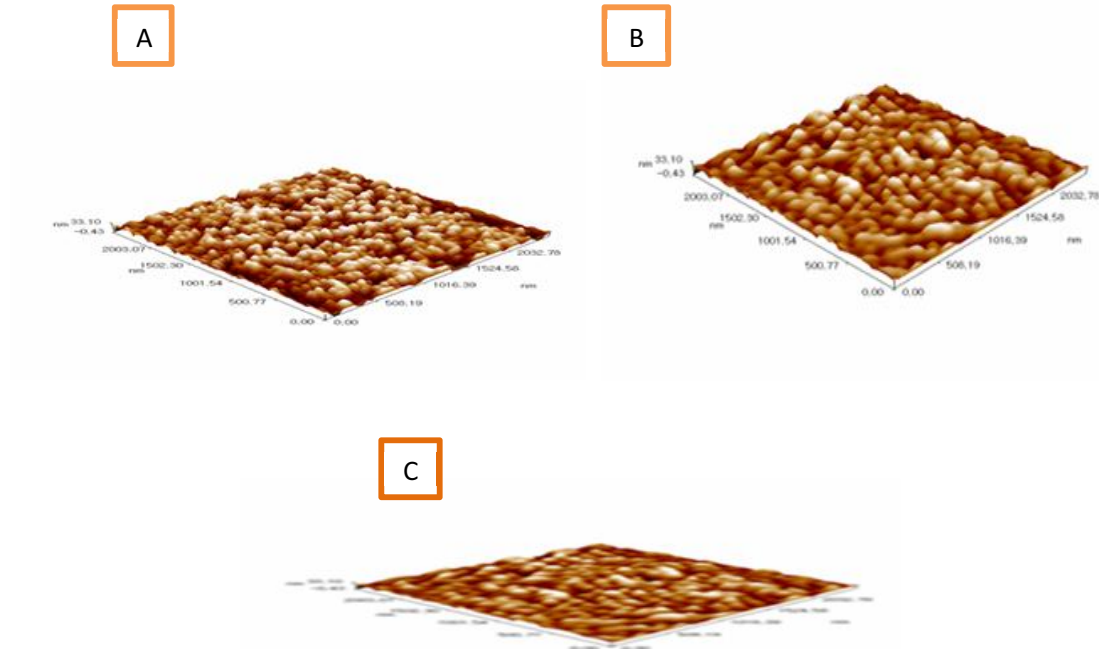


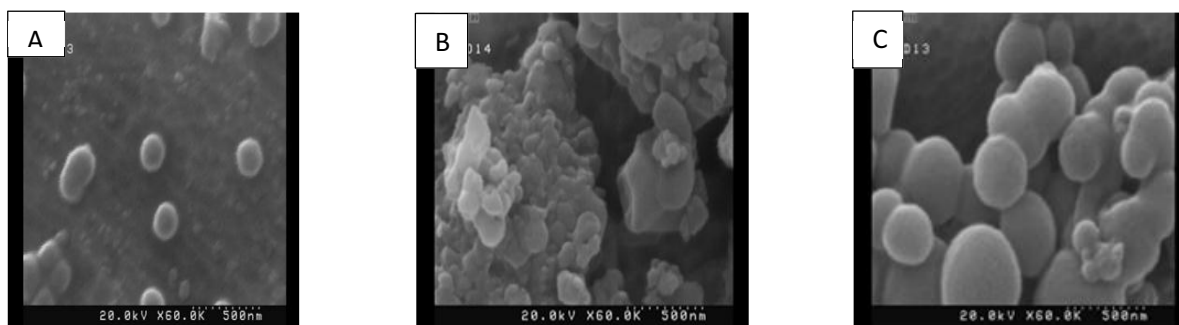
Figure4: AFM 3D image of (A) stainless steel coated POSPAEA without nano material (B) stainless steel coated POSPAEA with Graphene (C) stainless steel coated POSPAEA with ZnO Nano

Table 1: Average Diameter, Average roughness (Ra) and Root Mean Square (RMS) values

coating	Avg. Diameter	Ra (nm)	RMS (nm)
POSPAEA	90.59	6.74	8.09
POSPAEA& Graphene	82.35	4.55	5.69
POSPAEA& ZnO	103.46	9.79	12

#### 4.2.3. Scanning electron microscope (SEM)

The SEM morphologies of 316L stainless steel coated POSPAEA with and without Nano materials (graphene and ZnO (Nano)) are shown in (Fig 5) the first SEM image for POSPAEA without nano material gave spherical grain with different sizes Spaced apart when the second SEM image gave agglomerate granular of the graphene with the polymer matrix coherent together [58] and the third SEM image of POSPAEA with ZnO Nano showed aggregates of the particles with irregular shapes and different sizes .



Fig(5) SEM image of (A) Stainless steel coated POSPAEA without nano material (B) Stainless steel coated POSPAEA with Graphene (C) Stainless steel coated POSPAEA with ZnO Nano

#### 4.2.4. Potentiostatic polarization measurements

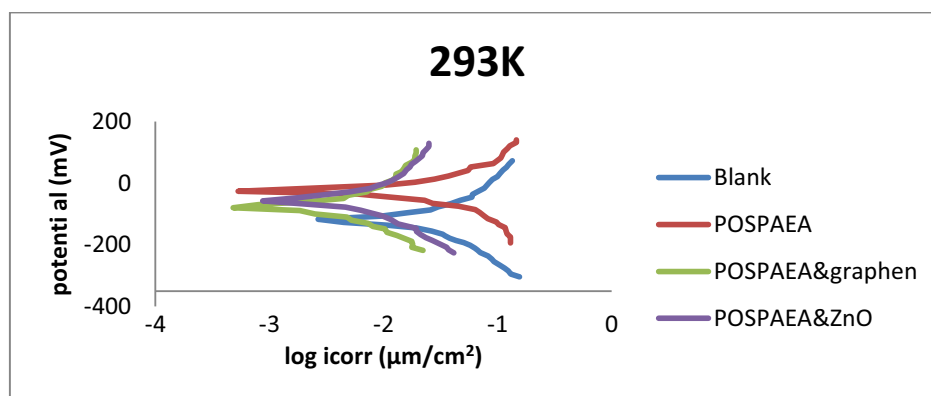
The influence of polymeric coating film on the anodic and cathodic polarization curves of 316L S-steel in (0.2) M HCl solution at temperature from 293 to 323K . The influence of adding various nanomaterial compound [Zno Nano, graphene] is appeared in Figure (6) for POSPAEA. The corrosion current density  $I_{corr}$  was determined by extrapolation of anodic and cathodic Tafel plot table (2) appeared the influence of polymer coating in presence and absence nano materials on the corrosion parameter of the 316Ls-steel electrode. These parameters including corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), anodic Tafel slope ( $b_a$ ) and cathodic Tafel slope ( $b_c$ ), weight loss, penetration loss, polarization resistance ( $R_p$ ) and protection efficiency (PE %). The relation determining the polarization resistance ( $R_p$ ) is shown in the following [59]

$$R_p = \frac{b_a b_c}{2.303 (b_a + b_c)} I_{corr} \dots\dots\dots (1)$$

While the protection efficiency (PE %) determined from the equation [60]

$$PE\% = \left[ 1 - \frac{I_{\text{corr}}}{I_{\text{corr}^0}} \right] 100 \dots \dots \dots (2)$$

Where:  $I_{\text{corr}^0}$ ,  $I_{\text{corr}}$  are the corrosion rate of uncoated and coated stainless steel respectively



Figure(6) Polarization plots of 316L S-steel coated with polymer and nano material in 0.2M HCl at 293K.

Table (2): Corrosion data of 316LS-steel in 0.2M HCl with and without coating

Coating	T/K	-E <sub>corr</sub> mV	I <sub>corr</sub> μA/cm <sup>2</sup>	-bc mV/Dec	ba mV/Dec	PE%	Weight loss g/m <sup>2</sup> .d	Penetration loss[mm/y]	R <sub>p</sub> Ω.cm <sup>2</sup>
Blank 0.2M HCl	293	116.7	18.42	188.7	159.8	-	1.48	2x10 <sup>-1</sup>	2039.681
	303	126	21.37	199.1	185.8	-	1.72	2.32x10 <sup>-1</sup>	1952.858
	313	206.6	24.35	207.7	220.5	-	1.96	2.65x10 <sup>-1</sup>	1906.821
	323	271.8	25.89	171.6	258.5	-	2.08	2.82x10 <sup>-1</sup>	1729.746
POSPAEA	293	26	3.44	45.8	48.4	81.32	2.77x10 <sup>-1</sup>	3.74x10 <sup>-2</sup>	2970.35
	303	49.8	6.02	84.7	91	71.8	4.84x10 <sup>-1</sup>	6.54x10 <sup>-2</sup>	3164.19
	313	52.4	9.13	116.1	134.3	62.5	7.35x10 <sup>-1</sup>	9.93x10 <sup>-2</sup>	2961.483
	323	64.1	10.98	144.5	151.2	57.6	8.84x10 <sup>-1</sup>	1.19x10 <sup>-1</sup>	2921.945
POSPAEA & Graphene	293	78	1.38	70.1	68.1	92.5	1.1x10 <sup>-1</sup>	1.5x10 <sup>-2</sup>	10848.86
	303	148.7	3.64	66.1	71.2	82.9	2.93x10 <sup>-1</sup>	3.96x10 <sup>-2</sup>	4088.986
	313	227	5.14	48.2	87.2	78.9	4.14x10 <sup>-1</sup>	5.59x10 <sup>-2</sup>	2622.333
	323	256.8	6.3	62.1	84.7	75.66	5.07x10 <sup>-1</sup>	6.85x10 <sup>-2</sup>	2469.531
POSPAEA & ZnO <sub>n</sub>	293	56.2	2.12	71.6	84.2	88.5	1.7x10 <sup>-1</sup>	2.3x10 <sup>-2</sup>	7925.522
	303	50.9	4.3	168.9	142.3	79.8	3.46x10 <sup>-1</sup>	4.68x10 <sup>-2</sup>	7798.886
	313	109	6.7	216.6	257.6	72.5	5.39x10 <sup>-1</sup>	7.29x10 <sup>-2</sup>	7625.6
	323	146.9	7.64	228.2	274.9	70.5	6.15x10 <sup>-1</sup>	8.31x10 <sup>-2</sup>	7086.777

In table (2) shows the shift in corrosion potential of the coated film POSPAEA to more positive values and corrosion current density decreased when the Nano materials adding to the monomer solution which indicate the inhibiting effect of these materials. When the POSPAEA film crafted with Nano material coated on the stainless steel the E<sub>corr</sub> shifted to the noble direction [61] and the R<sub>p</sub> values are increased

greater than uncoated stainless steel. This indicates the corrosion resistant feature of the coating.

#### 4.2.5. Kinetic and thermodynamic of activation parameters

The influence of temperature on the corrosion rate for 316L stainless steel in the absence and presence different coating of POSPAEA at temperatures from 293 to 323K were obtained by using potentiostatic measurement to examine the influence of temperature on the corrosion process for coated and uncoated stainless steel the Arrhenius equation below mentioned eq (3 and 4) was used in fig (7) to calculate the activation energies [62].

$$C.R = A \exp\left(\frac{-E_a}{RT}\right) \times 100 \quad \text{..... (3)}$$

$$\log C.R = \log A - \frac{-E_a}{2.303 RT} \quad \text{..... (4)}$$

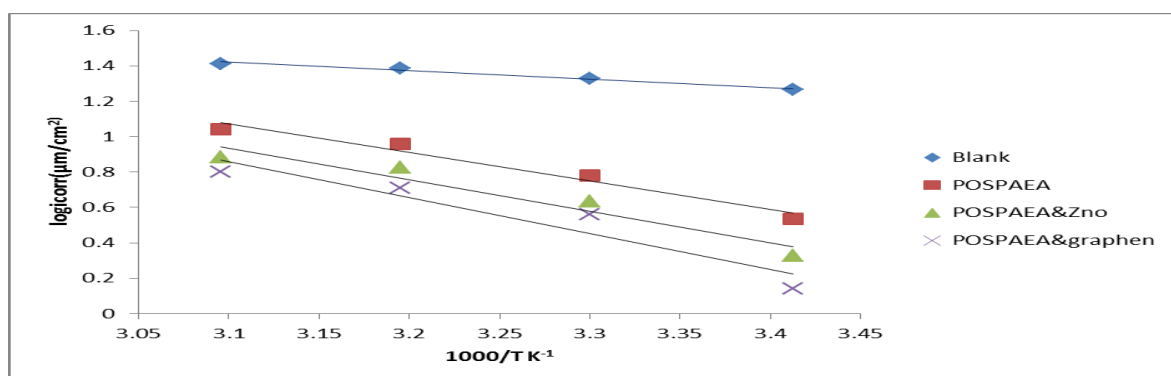


Figure (7) Arrhenius Plot of log CR versus 1/T for 316L S-steel in 0.2M HCl in the absence and presence coating

The values of the entropy of activation  $\Delta S^*$  and the enthalpy of activation  $\Delta H^*$  for the corrosion of uncoated and coated stainless steel were estimated from (Fig8) from transition state equation (5,6)

$$C.R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad \text{..... (5)}$$

$$\left(\log \frac{C.R}{T}\right) = \log \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \quad \text{..... (6)}$$

While the values of the activation free energy  $\Delta G^*$  was calculated using the following equation (7) [63]

$$\Delta G^* = \Delta H^* - T\Delta S^* \dots\dots\dots (7)$$

Where( C.R) is the corrosion rate, ( A )the pre- exponential factor, (Ea )is the apparent the activation energy ,( T) the absolute temperature ,( R )the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),( h) Plank's constant (6.626176 x 10<sup>-34</sup>JS), (N) is Avogadro's number (6.022 x 10<sup>23</sup> mol<sup>-1</sup>), (ΔS\*) the entropy of activation , (ΔH\*) the enthalpy of activation and ( ΔG\*) the Gibbs free energy.

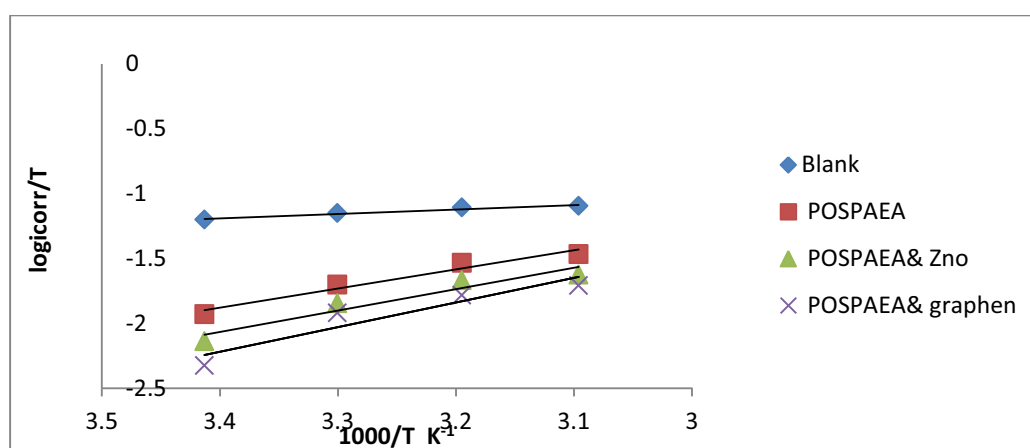


Figure (8) Arrhenius plots of log CR/T vs. 1/T for 316LS-steel in 0.2M HCl in the absence and presence coating

The calculated kinetic and thermodynamic values were represented in Table (3), in this table the results show that the increase in the activation energies in the presence of POSPAEA film indicates the higher protection efficiency of the coating. The values of activation energies are increase with addition different coating indicating that increases in the energy barrier of the corrosion reaction. the positive signs of enthalpies of activation of corrosion transition state reaction of stainless steel in 0.2M HCl with various coating film at temperature from 293to 323K indicate the endo thermic nature for the reaction. The large negative values of entropy of activation indicate that formation ordered stable film in the presence of inspected coating on the stainless steel surface[64-65]. The calculated  $\Delta G^*$  values takes positive sign , showed small change with rise in the temperatures , indicates that the probability of formation the activated complex decreased with increasing temperature because it's not stable and the  $\Delta G^*$  value for coated film showed that in the activated corrosion complex become less stable as compared to the uncoated stainless steel

Table (3): Activation parameters  $E_a$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  for the coated and non-coated 316L S-steel dissolution in 0.2M HCl

Coating	$R^2$	$E_a$ $\text{kJ.mol}^{-1}$	A/Molecule. $\text{Cm}^{-2}.\text{S}^{-1}$	$R^2$	$\Delta H^*$ $\text{KJ. K}^{-1}.\text{mol}^{-1}$	$-\Delta S^*$ $\text{J .K}^{-1}.\text{mol}^{-1}$	$\Delta G$ $\text{KJ. K}^{-1}.\text{mol}^{-1}$
HCl Blank	0.9789	9.1026	$4.721 \times 10^{26}$	0.9580	6.5464	198.1117	64.593
							66.574
							68.555
							70.536
POSPA EA	0.9664	30.8497	$7.023 \times 10^{29}$	0.9598	28.2950	137.3558	68.540
							69.913
							71.287
							72.661
POSPA EA & Graphen	0.9008	38.9357	$87.789 \times 10^{29}$	0.8874	36.3777	116.3667	70.473
							71.637
							72.800
							73.964
POSPA EA & ZnO <sub>n</sub>	0.9325	34.0283	$16.785 \times 10^{29}$	0.9214	31.472	130.1239	69.599
							70.899
							72.200
							73.502

## 5. Conclusion

The electro polymerized POSPAEA coating on 316LS-steel was found to protect efficiently in 0.2 M HCl solution. The protection efficiency of polymer increases with adding Nano materials to monomer solution exceptionally with graphene and decreases with increases temperature from (293 to 323) K . The values of corrosion potential of coated film on stainless steel shifted to the noble direction. The values of activation energies are increase with addition different coating than that of uncoated stainless steel indicating more energy barrier. The enthalpies of activation of stainless steel with various coating film at different temperature are positive values indicating to endo thermic reaction , the entropy of activation are large negative values indicate that formation ordered stable film in the presence of inspected coating on the stainless steel surface and the Gibbs free energy values takes positive sign showed small change with rise in the temperatures , indicates that the probability of formation the activated complex decreased with increasing temperature. The AFM analysis for POSPAEA with and without Nano materials(Graphene ,ZnO) shows the surface roughness decreases with decreases in the diameter average and the smooth and uniform surfaces act a good barrier favorably effect for protection the coatings from corrosion, the surface morphology of stainless steel coated

POSPAEA with and without nano material indicated that the protection efficiency against corrosion increase with increase the interaction between the polymer and nano material .

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