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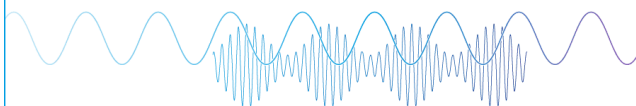
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# Synthesis, Identification and Experimental Studies for Carbon Steel Corrosion in Hydrochloric Acid Solution for Polyimide Derivatives

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**Abstract.** The present work reports the synthesis of polyimides (polymer A, polymer B, Polymer C). These polymers characterized by Fourier Transform Infrared Spectroscopy (FT-IR). Corrosion measurements for carbon steel (C.S) in hydrochloric acid (HCl)(1M) solution (blank) and inhibitors (polymer A, polymer B, Polymer C)(50 ppm) solutions were studied at temperature range (293-323)K by electrochemical polarization technique. Kinetic and thermodynamic activation parameters ( $E_a$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$ ) for blank and inhibitors solutions were calculated.

**Keywords:** Polyimides, Corrosion, Carbon steel, Hydrochloric acid, Electrochemical polarization technique

## INTRODUCTION

Corrosion is defined as the interaction of metals with their environment [1], it also defined is the surface damage or metal deterioration in the aggressive environment. It was involved chemical or electrochemical oxidation processes, the metal was transferred electrons to its environment and undergoes to valence change from zero to a positive value. The environment involved gas, liquid and hybrid soil-liquid. These environments called electrolytes and have their conductivity for electron transfer [2]. A corrosion inhibitor is a chemical compound adsorbed on metal or alloy surface to give film in order to isolate the surface of the alloy from reaction with the environment or by lowering the ions which attack the metal surface [3,4]. The majority of the productive corrosive inhibitors are organic compounds that include different heteroatoms like oxygen, sulfur or nitrogen atoms in their structures. The inhibition efficiencies of organic compounds is depended on the structure and chemical assets of the film designed on the alloy. Organic compounds are used for their efficiencies as corrosion inhibitors and those containing nitrogen have been frequently [5-7]. The choice of these compounds is due to: a) are extremely have large molecular weights, b) include functional polar (such as  $-C=O$ ,  $C=N$ ) and wide connection in the form of aromatic ring among which they can adsorb on surface of alloy[8]. The objective of this paper is study the inhibitive behavior of these investigated organic compounds in the direction of the corrosion of C.S in (1M) HCl by electrochemical polarization technique.

## MATERIALS AND METHODS

### Synthesis of 4-(1-((5 (4-Nitrophenyl)-1,3,4-Thiadiazol-2-Yl) Imino) Ethyl) Aniline (Compound 1)

Synthesis of Schiff bases [comp.1] was performed by refluxing of (0.01 mol, 2.22 g) of (5-(4-nitrophenyl)-1,3,4-thiadiazol-2-amine) with (0.01 mol, 1.35 g) of 4-amino acetophenone dissolved in (30 mL) of absolute ethanol with added of few drops of glacial acetic acid for 7hrs. with stirring. The resulted solid was filtered, dried then purified by recrystallization from acetone [9].

### Synthesis Of of 4-((4-(1-((5-(4-Nitrophenyl)-1,3,4-Thiadiazol-2-Yl)Imino-4-Oxobut-2-Enoic Acid (Compound 2)

A solution of (0.01 mol, 3.39 g) of Schiff base [comp.1] dissolved in (25 mL) acetone was added dropwise to the solution of (0.01 mol, 0.98 g) of maleic anhydride dissolved in (25 mL) of acetone with stirring. The resulted mixture was stirred for additional 3hrs. the formed precipitate was filtered, washed with acetone then ether, dried and purified by recrystallization from ethanol [10].

### Synthesis of N-(4-(1-((5 (4-Nitrophenyl)-1,3,4-Thiadiazol-2-Yl)Imino)Ethyl)Phenyl) Maleimide (Compound 3)

(0.005 mol, 2.18 g) of comp.2 dissolved in (25 ml) acetic anhydride with (5-10) % by weight of anhydrous sodium acetate, the mixture was refluxed with stirring for 3hrs. The resulted solution was cooled then poured into crushed ice with vigorous stirring. The obtained solid precipitate was filtered, washed with water, dried and purified by recrystallization from acetone [11].

### Synthesis of Homopolymer (A)

In a screw capped polymerization bottle (0.001 mol) of comp.3 was dissolved in (15 mL) of THF then (0.0002 g) of initiator (Azobisisobutyronitrile) was added, then the bottle was flushed with nitrogen and stoppered. The mixture was heated to (70C°) for 4hrs. then the resulted solution was poured into (25 mL) of methanol, the precipitated polymer was filtered, washed with methanol and dried [12].

### Synthesis of Copolymer B and C

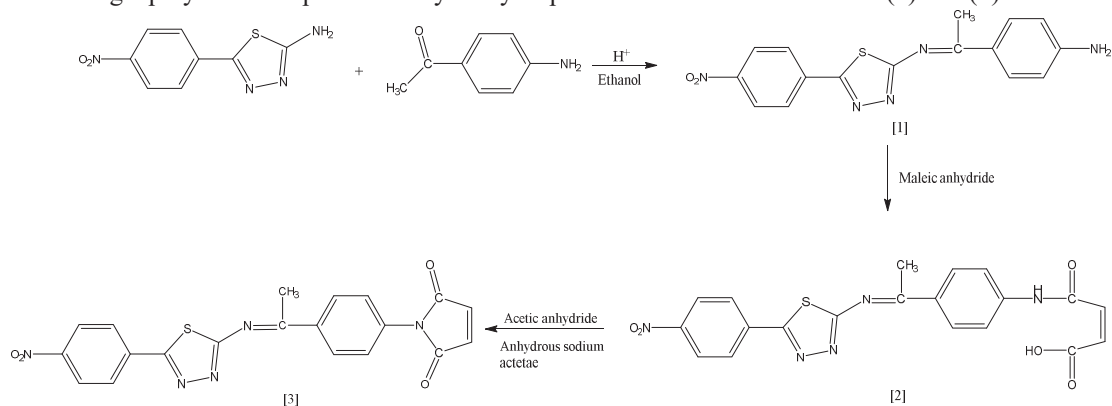
In a screw capped polymerization bottle equimolar amounts of compounds (3) (0.001mol) and (acrylonitrile or methyl acrylate) were dissolved in (15mL) of THF then (0.0002g) of initiator (Azobisisobutyronitrile) was added as initiator. Then the bottle was flushed with nitrogen and stoppered then maintained at(75C°) for 4hrs. the resulted solution was poured into (25mL) of methanol and the precipitated copolymer was filtered, washed with methanol and dried [12].

## CORROSION MEASUREMENT

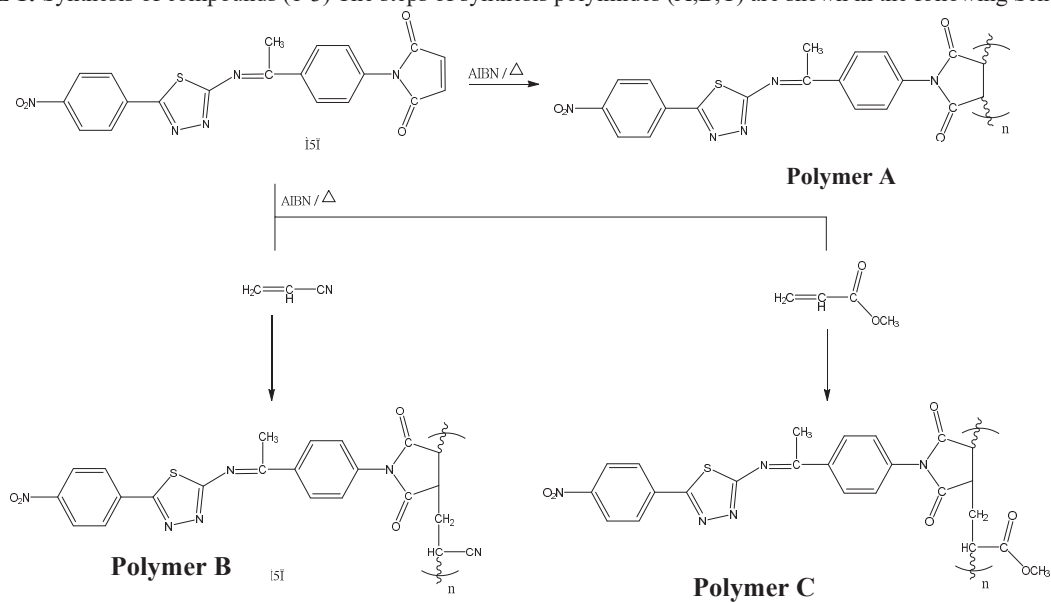
The potentiostat set up includes a Host computer, thermostat, magnetic stirrer, Mat lab (Germany, 2000), potentiostat, and galvanostat. The cell is (1 L) capacity made of Pyrex consist of internal and external bowls. The electrochemical corrosion cell is three electrodes. Carbon steel as a working electrode used to determine the potential of it according to the reference electrode, an auxiliary electrode is a platinum with length (10 cm) and reference electrode a silver-silver chloride (Ag/AgCl, 3.0 M KCl). The working electrode was immersed in the test solution for 15 min to establish steady state open circuit potential (Eocp), then electrochemical measurements were performed in a potential range of ( $\pm 200$ ) mV. All tests were carried out at the temperature of (293-323 K) controlled by using a cooling-heating circulating water bath.

## RESULTS

Synthesis of target polymers was performed by many steps which are shown in Scheme (1) and (2).



**SCHEME 1:** Synthesis of compounds (1-3) The steps of synthesis polyimides (A,B,C) are shown in the following Scheme:



**SCHEME 2:** Synthesis of polymers (A,B,C)

The physical properties for compounds (1-3) are shown in TABLE 1.

**TABLE 1:** Physical properties for compounds (1-3)

Comp.No.	Compound structure	Color	Melting point °C	Yield %	Recrystallization solvent
1		Yellow	112-115	80	Acetone
2		Pale yellow	244-246	87	Ethanol
3		Brown	185-188	83	Acetone

FT-IR spectra for compounds (1-3) showed the following:

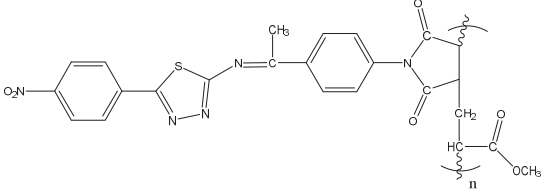
Compound 1 showed two absorption bands at (3334 and 3298)  $\text{cm}^{-1}$  were due to asymmetric and symmetric stretching vibration of (-NH<sub>2</sub>) and other absorption bands at (1639 and 1593)  $\text{cm}^{-1}$  which are due to  $\nu(\text{C}=\text{N})$  imine,  $\nu(\text{C}=\text{C})$  aromatic respectively. Compound 2 showed absorption bands at (3448, 3425)  $\text{cm}^{-1}$  due to  $\nu(\text{O}-\text{H})$  carboxyl and  $\nu(\text{N}-\text{H})$  amide, and absorption bands at (1710, 1695 and 1631)  $\text{cm}^{-1}$  which are due to  $\nu(\text{C}=\text{O})$  carboxyl,  $\nu(\text{C}=\text{O})$  amide and  $\nu(\text{C}=\text{N})$  imine respectively. Compound 3 showed characteristic clear absorption bands at (1772 and 1718)  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  imide, and other absorption bands at (1631 and 1600)  $\text{cm}^{-1}$  which are due to  $\nu(\text{C}=\text{N})$  imine,  $\nu(\text{C}=\text{C})$  aromatic respectively [13-15]. Details of FT-IR spectra data are listed in TABLE 2.

**TABLE 2:** FT-IR spectral data ( $\text{cm}^{-1}$ ) for compounds (1-3)

Comp. No.	$\nu(\text{O}-\text{H})$ $\nu(\text{N}-\text{H})$	$\nu(\text{C}-\text{H})$ Arom.	$\nu(\text{C}=\text{O})$ Acid	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{O})$ Amide	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$ Imide	$\nu(\text{C}=\text{N})$
1	3334	3004	-	-	-	1593	-	1639
2	3448 3425 3282	3004 3055	1710	-	1695	1573	-	1631
3	-	3024	-	1772	-	1600	1371	1631

**TABLE 3:** Physical properties for polyimides (A, B, C)

polymer	Polymer structure	Color	Softening point °C	Conv.Ratio	Purification
A		Brown	205-216	85	By dissolving in THF then precipitation by methanol
B		Brown	133-148	81	

Polymer	Polymer structure	Color	Softening point °C	Conv.Ratio	Purification
C		Brown	103-115	87	

The physical properties for polyimides (A,B,C) are shown in TABLE 3.

FT-IR spectrum for polyimides (A,B,C) showed the following:

Polymer A showed absorption bands at (2830-2910)  $\text{cm}^{-1}$  due to  $\nu(\text{C-H})$  aliphatic which showed clear proof for success of polymer formation. Other absorption bands at (1772 and 1718)  $\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  imide and at (1633)  $\text{cm}^{-1}$  which are due to  $\nu(\text{C=N})$  imine. Polymer B showed important absorption bands at (2243)  $\text{cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{N})$  and absorption bands at (1745, 1712)  $\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  imide, other absorption bands at (2929)  $\text{cm}^{-1}$  due to  $\nu(\text{C-H})$  aliphatic. Polymer C showed absorption bands at (1730)  $\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  ester and absorption bands at (1774, 1710)  $\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  imide, other absorption bands at (2860-2922)  $\text{cm}^{-1}$  due to  $\nu(\text{C-H})$  aliphatic [13-15]. Details of FT\_IR spectra are listed in TABLE 4.

TABLE 4: FT-IR spectral data ( $\text{cm}^{-1}$ ) for polyimides (A, B, C).

Poly. No.	$\nu(\text{C-H})$ Arom.	$\nu(\text{C-H})$ Aliphatic.	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C=O})$ Imide	$\nu(\text{C=N})$	$\nu(\text{C=O})$ Ester	$\nu(\text{C-N})$ Imide	$\nu(\text{C-O-C})$ Ester
A	3030	2830 2910	-	1772 1718	1633	-	1367	-
B	3004	2929	2243	1745 1712	1630	-	1346	-
C	3074	2860 2922	-	1774 1710	1628	1730	1373	1242 1149

## POLARIZATION CURVES

The corrosion parameters were evaluated from the resulting data in TABLE 5 and Fig. 1. The corrosion current density ( $i_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) were obtained by the extrapolation of the cathodic and anodic Tafel in absence and presence the inhibitors molecules in HCl solution. The anodic ( $b_a$ ) and cathodic ( $b_c$ ) Tafel slopes were also calculated from Fig. 1. TABLE 5 shows the resulting data of the corrosion potential  $E_{\text{corr}}$  (mV), corrosion current density  $i_{\text{corr}}$  ( $\mu\text{A}/\text{cm}^2$ ), cathodic and anodic Tafel slopes  $b_c$  and  $b_a$  (mV/Dec), polarization resistance  $R_p$  ( $\Omega/\text{cm}^2$ ), weight loss WL ( $\text{g}/\text{m}^2.\text{d}$ ), penetration loss PL (mm/y), and protection efficiency PE%. The data in TABLE 5 show that the corrosion current density ( $i_{\text{corr}}$ ) was generally increased with temperature. Tafel plot reveals that  $E_{\text{corr}}$  for C.S in the presence the inhibitors shifts to a higher (noble) position compared with blank solution, implying that the protection acts as an anodic protection [16]. The inhibition efficiency (%IE) was calculated by the following equation [17]:

$$\%IE = \frac{(i_{\text{corr}})_0 - (i_{\text{corr}})}{(i_{\text{corr}})_0} * 100 \quad (1)$$

Wehre ( $i_{\text{corr}})_0$  is the corrosion current density in the Absence of Inhibitors, ( $i_{\text{corr}}$ ) is the corrosion current density in the presence of inhibitors. The synthesized polyimides showed good inhibition efficiencies and that due to containing imide groups, also contain heterogeneous rings (thiazadiazole ring), also contain sulfur, oxygen, nitrogen which form with metal a complex that adsorb on the surface of alloy and protect it from corrosive media [8].

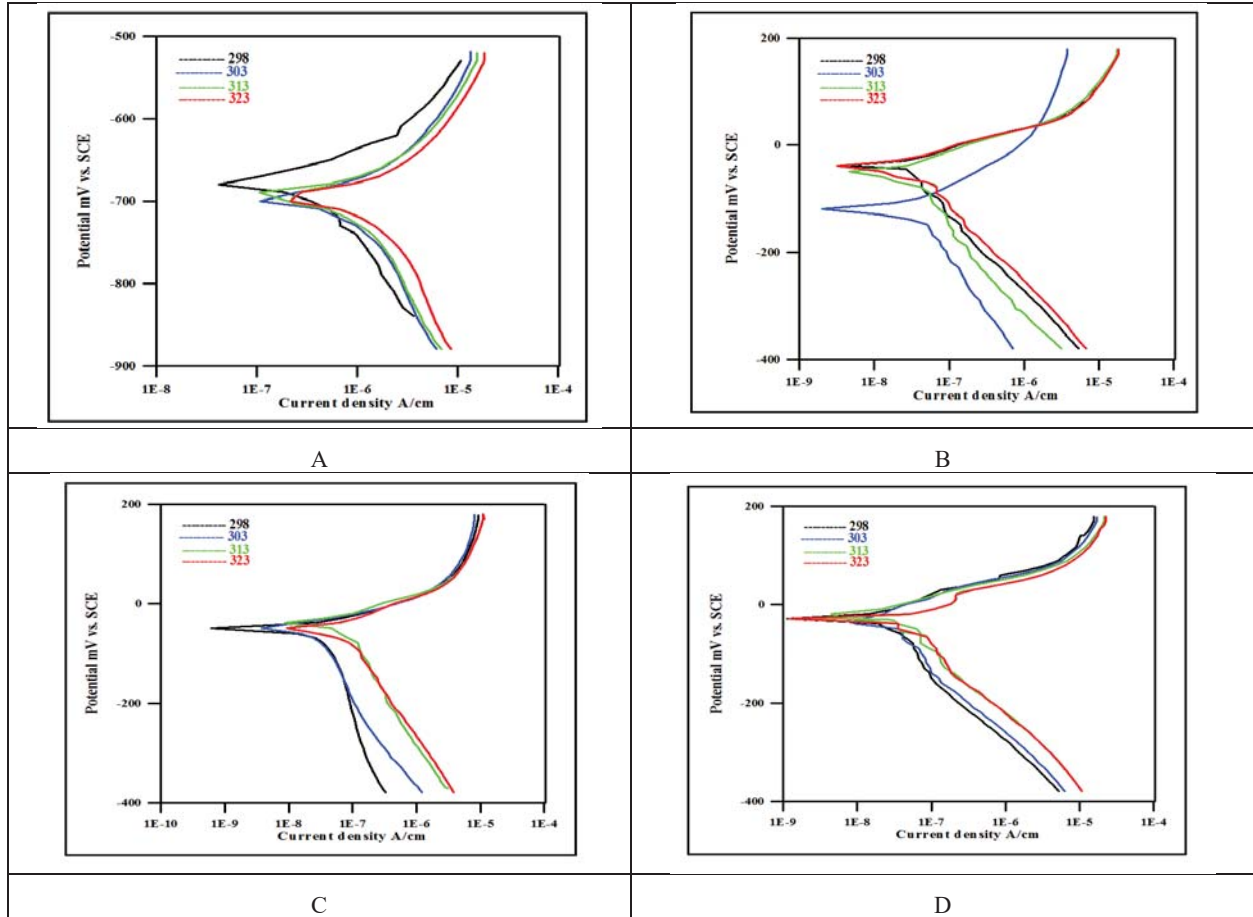


FIGURE 1: Polarization curves for corrosion of a) Blank, b) polymer A, c) Polymer B, d) polymer C

TABLE 5: Corrosion parameters for blank and inhibitors solutions at temperature range (293-323) K

	T(K)	-E <sub>corr</sub> (mV)	i <sub>corr</sub> ( $\mu$ A/cm <sup>2</sup> )	$-\beta_c$ (mV/sec)	$\beta_a$ (mV/sec)	WL (g/m <sup>2</sup> .d)	PL (mm/y)	IE%
Blank	293	700.2	507.43	-198.8	98.9	127	5.89	-
	303	700.2	573.79	-122.8	85.9	143	6.66	-
	313	696.2	601.22	-127.7	79.1	150	6.98	-
	323	700.2	663.15	-90.3	74.2	166	7.70	-
Polymer A	293	36.2	20.64	-121.3	41.7	5.16	0.240	95.93
	303	118.2	26.75	-144.8	73.2	6.69	0.311	95.33
	313	46.7	29.16	-182.5	60.0	7.29	0.338	95.14
	323	37.0	34.29	-154.3	52.3	8.57	0.398	94.82
Polymer B	293	51.2	14.09	-90.6	33.4	3.52	0.163	97.22
	303	49.6	19.28	-145.7	37.9	4.82	0.224	96.63
	313	39.8	22.94	-69.6	36.2	5.74	0.266	96.18
	323	53.2	29.70	-71.5	42.9	7.42	0.345	95.52
Polymer C	293	29.1	16.06	-88.4	50.5	4.02	0.186	96.83
	303	29.1	23.78	-154.0	55.3	5.95	0.276	95.85
	313	14.9	33.25	-157.0	44.1	8.31	0.386	94.46
	323	-34.7	39.07	-139.2	55.1	9.77	0.453	94.10

## KINETIC AND THERMODYNAMIC ACTIVATION PARAMETERS

Thermodynamic activation parameters involved the activation energy  $E_a$ , enthalpy of activation  $\Delta H^*$ , and entropy of activation  $\Delta S^*$ , as calculated by using the Arrhenius equation and its alternative formulation that is called the transition state. The activation energy was determined from the plot that represents the relationship between  $\text{Log C.R}$  and the reciprocal of the absolute temperature ( $1/T$ ) [18], as shown in Fig. 2.

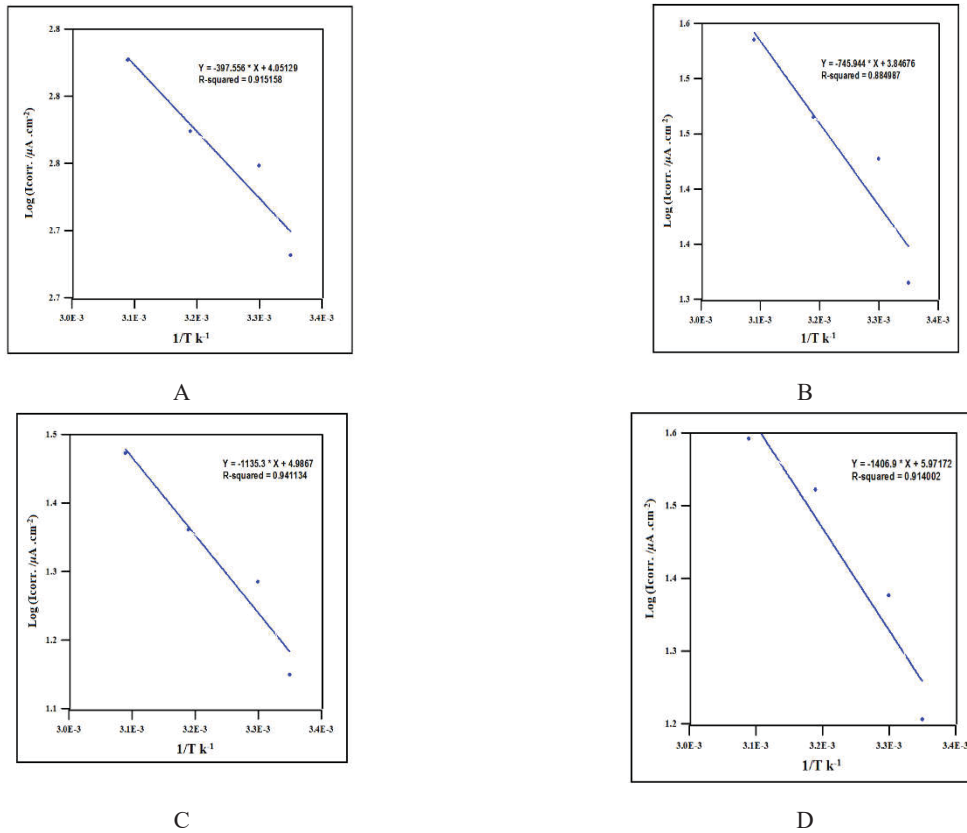
$$\text{Log C.R} = \text{Log A} - \frac{E_a}{2.303RT} \quad (2)$$

Where C.R: corrosion rate, A: pre-exponential factor,  $E_a$ : Activation energy, R: Gas constant ( $8.315 \text{ JK}^{-1}\text{mol}^{-1}$ ), T: Absolute temperature (K). While, the transition state is expressed in the following equation [19]:

$$\text{Log} \frac{\text{C.R}}{T} = \text{Log} \left[ \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} \right] - \frac{\Delta H^*}{2.303RT} \quad (3)$$

Where N: Avagadrous number ( $6.022 \times 10^{23} \text{ mol}$ ), h: Planks constant ( $6.62 \times 10^{-34} \text{ J.S}$ ). The entropy of activation  $\Delta S^*$  and enthalpy of activation  $\Delta H^*$  were determined from the plot that represents the relationship between  $\log (\text{C.R}/T)$  and the reciprocal of the absolute temperature ( $1/T$ ), as shown in Fig. 3. Where the slope represents ( $-\Delta H^*/2.303RT$ ) and the intercept represents ( $\text{Log} (R/Nh) + \Delta S^*/2.303R$ ). The free energy of activation was determined from the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$



**FIGURE 2:** Plot of  $\log i_{\text{corr}}$  vs.  $1/T$  for a) Blank, b) polymer A, c) polymer B, d) polymer C



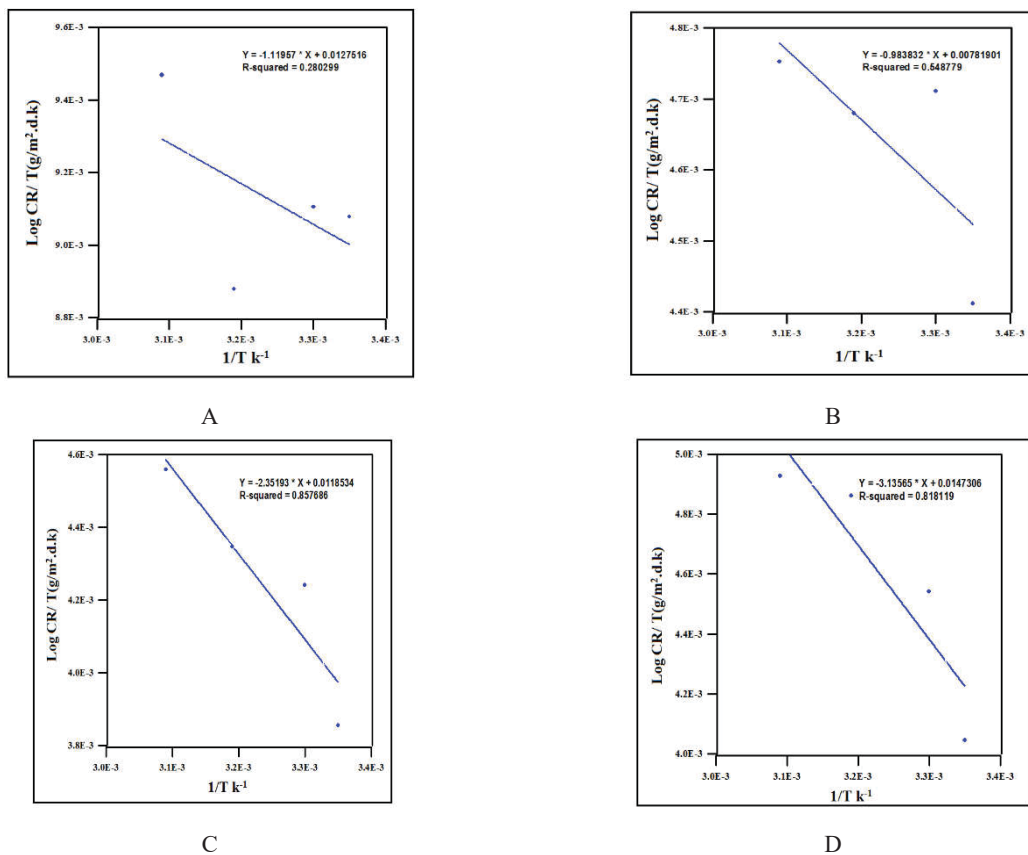


FIGURE 3: Plot of  $\log i_{corr}/T$  vs.  $1/T$  for a) Blank, b) polymer A, c) polymer B, d) polymer C

TABLE 6: Transition state thermodynamic parameters at different temperatures for the corrosion of blank and inhibitors solutions at temperature range (293-323) K

Sample	T(K)	Ea	$\Delta H^*$	$\Delta S^*$	$\Delta G^*$
		(kJ/mole)	(kJ/mol)	(J/mol.K)	(kJ/mol)
Blank	293	7.612	0.021	-1.060	0.336
	303				0.342
	313				0.352
	323				0.363
Polymer A	293	14.282	0.018	-1.065	0.335
	303				0.340
	313				0.351

Sample	T(K)	Ea	$\Delta H^*$	$\Delta S^*$	$\Delta G^*$
		(kJ/mole)	(kJ/mol)	(J/mol.K)	(kJ/mol)
Polymer B	323				0.361
	293				0.361
	303	21.737	0.045	-1.061	0.366
	313				0.377
	323				0.387
Polymer C	293				0.375
	303	26.938	0.060	-1.058	0.380
	313				0.391
	323				0.401

The results show that the thermodynamic activation parameters ( $E_a$  and  $\Delta H^*$ ) for the C.S in the inhibitors solutions are higher than those for the blank solution. This indicates an increase in the energy barrier. The values of the entropy of activation for C.S in the inhibitors and blank solutions are negative, indicating that the activated complex in the rate-determining step was achieved in an association rather than a dissociation step, along with a decreased disordering which occurs upon moving from reactants to activated complex [20]. The free energy activation had positive values, as shown in TABLE 6. There is almost a small change is shown with an increase temperature, indicating that the activated complex was not stable, and the probability of its formation was decreased with increasing of temperature [21].

## CONCLUSIONS

The corrosion current density ( $i_{corr}$ ) decreased after adding the inhibitors into blank solution. Tafel plots revealed that corrosion potential ( $E_{corr}$ ) of the C.S in presence of the inhibitors shifts to a higher position as compared with blank solution, implying these inhibitors acts as an anodic protection. Inhibition efficiency (IE%) was decreased with increasing temperature for all inhibitor's solutions. polymer B has higher IE% than other inhibitors at 293K due to containing imide groups, also contain heterogeneous rings (thiazidazole ring), also contain sulfur, oxygen, nitrogen which form with metal a complex that adsorb on the surface of alloy and protect it from corrosive media .

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