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Inhibition of Steel Acid Corrosion by Newly Synthesized Organic Compound

W. I. Eldougdoug, Shereen A. Abdelkader, N. Fouad, Basma Khedr, A. Y. El-Etre
Chemistry department, Faculty of science, Benha university, Benha, Egypt

Abstract

A novel N,N'-(azanediylbis(ethane-2,1-diyl))dinicotinamide was prepared by the reaction of methylnicotinate with diethylenetriamine. The chemical structure of the prepared compound was confirmed by FTIR and ^{1}HNMR. The prepared compound was examined as corrosion inhibitor for carbon steel in hydrochloric acid solutions using weight loss, potentiodynamic polarization and electrochemical Impedance Spectroscopy Techniques. Tafel polarization studies showed that the surfactant is mixed type inhibitor. The adsorption of the prepared compound on to the surface of carbon steel in 1 M HCl obeys the Langmuir isotherm. Also, activation thermodynamic parameters such as Ea, ΔH^* and ΔS^* were calculated using Arrhenius and transition state equations and discussed.

Keywords: organic synthesis, corrosion inhibitor, C-steel
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1. Introduction

Corrosion process plays an important role in the field of economics and safety. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Various types of steel including carbon steel are used in different industries (chemical and electrochemical industries, nuclear, power, petroleum, and food industry), and in daily life. However, carbon steel suffers from a certain type of corrosion within some environments. For this cause, the electrochemical properties of carbon steel are the subject of many studies. Hydrochloric acid is widely used as aggressive solution to remove unwanted scale and rust in many industrial processes. Due to the aggressiveness of acids, corrosion can be minimized by addition of corrosion inhibitors in small concentrations [1–7]. Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulfur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surfaces [8-15]. organic inhibitors can be used as concrete admixtures or in repair products to delay the onset of corrosion or to reduce the rate of corrosion of reinforcing steel in concrete structures. The inhibiting properties are documented in solution and in concrete. The interaction mechanism of the inhibitors with a steel surface has been studied using sophisticated surface analytical methods [16].

The aim of this work is to study the effect of the synthesized amid compound on the corrosion inhibition of carbon steel in 1 M HCl solution using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss methods.

2. Experimental

2.1. Materials

Diethylenetriamine purchased from Sigma-Aldrich Chemicals Co., Nicotinic acid methanol, toluene, Conc. Sulphuric, hydrochloric acid are higher grades, from AL-Nasr Chemicals Co. sodium carbonate were purchased from Algomhoria Chemicals Co.

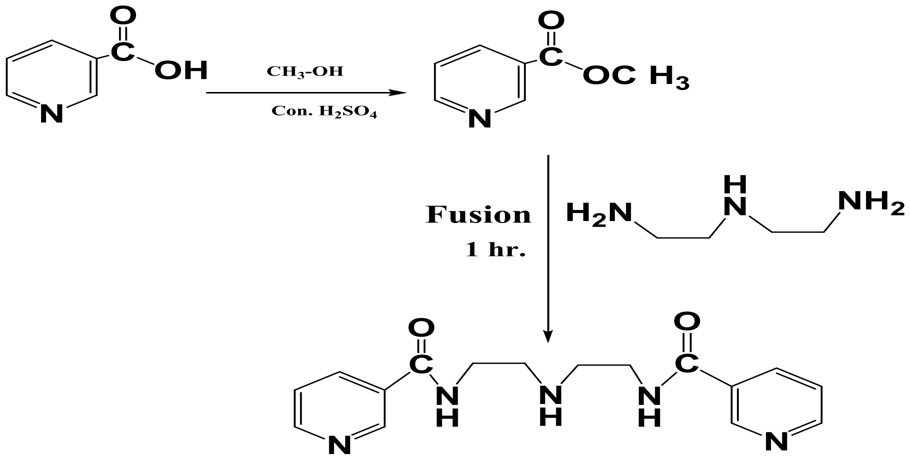
Carbon steel sample [Ferro(Fe), C (0.42-0.50 %), Si (< 0.40%), Mn(0.5-0.8%), P(< 0.045 %), S(< 0.045 %), Cr (< 0.4 %), Mo(< 0.1 %), Ni (0.4 %), -{Cr + Mo + Ni = < 0.63 %}] was purchased from International chemical Co.

2.2. Methods

2.2.1. Synthesis

Preparation of methyl nicotinate: Nicotinic acid (12.3 g; 0.1mol.) was esterified by refluxing with methanol (50 ml.) in presence of Conc. H_2SO_4 as catalyst (4 %) for about 15 hrs., followed by neutralization with sodium carbonate (15 % Solution), The obtained ester was extracted with chloroform, washed by distilled water three times and dried using anhydrous sodium sulphate followed by filtration. The extract distilled off to remove the chloroform to obtain white crystalline product (yield 76.67 %, m. p. 37-39 °C) [17].

Preparation of amino-nicotinodiamide derivative: The nicotino-diamide derivative was prepared by reacting methylnicotinate (2.74 g; 0.02 mol.) was reacted diethylenetriamine (1.46 g;0.01 mol.) through fusion in sand path for about one hour. Then left to be cooled over night to obtain final product as Reddish Brown color solusion [yield 80 %, m. p. 78-80° C] [18]. [Cf. Scheme (1)].



Scheme (1)

2.2.2. Weight loss technique

Steel specimens with dimensions of 2.4 x 0.6 x 2 cm were immersed in 1 M HCl in a closed beaker with and without the addition of different concentrations of inhibitor for 24 h at 25–70 °C. The concentration of the acid was adjusted by titration against a standard solution of sodium carbonate. Prior to each experiment, the surface of every specimen was mechanically polished with different grades of emery papers, cleaned with acetone and distilled water then dried at room temperature before use. The inhibition efficiency (η) and the fraction of surface covered by the additive (θ) were calculated using the following equations, respectively:

$$\eta = \left(\frac{W_f - W_i}{W_f}\right) x\ 100$$

$$\theta = \left(\frac{W_f - W_i}{W_f}\right)$$

where W_f and W_i are weight loss in free and inhibited solutions, respectively.

22.3. Electrochemical measurements

A three-electrode cell with platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode, was used for the electrochemical measurements. steel working electrode is a rode impeded in a glass tube with Araldite leaving an exposed bottom side with an area of 1.0 cm^2 contacted to the corrosive solution. The exposed surface was abraded with different grades of emery papers, rinsed with distilled water and acetone then dried between two filter papers, and inserting in the test solution. The electrode was lifted in the test solution until it reaches a steady-state potential value before starting the measurements. Corrosion parameters were obtained using Metrohm potentiostat supported with Nova software for calculations. The potentiodynamic polarization measurements were obtained using a scan rate of 2 mVs^{-1} at 25 ± 1 °C or other mentioned temperatures. The inhibition efficiency (η) obtained from electrochemical polarization and impedance spectroscopy were calculated using the following equations, respectively:

$$\eta = \left(\frac{I_f - I_i}{I_f}\right) x\ 100$$

where, I_f and I_i, are corrosion current density for the free and inhibited solutions.

3. Results and discussion

Synthesis of nictino-diamine was prepared by reacting methyl ester by fusion method. The chemical structure of the synthesized was confirmed by FTIR and 1HNMR.

The synthesized amide shows bands at 3289 cm-1 (νNH stretching), 3072 cm-1 (νCH aromatic stretching), 2944 cm-z and 2839 cm-1 (νCH aliphatic chain), 1649 cm-1 (νC=O amide), 1550 cm-1 (νC=C aromatic stretching), 1597 cm-1 (νNH amide bending), 1473 cm-1 (νCH2 bending), 1313 cm-1 (νC–N aryl stretching), 1164 cm-1 (νC–N alkyl stretching), 833 cm-1 (νCH para bending), 709 cm-1 (νCH ortho bending) Fig (1).

The data of ^{1}H-NMR spectra confirm the expected hydrogen proton distribution in the synthesized amide δ (ppm):

1.24 (2H, $CONHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH$ CO), 2.7 (4H,$CONHCH_2CH_2NHCH_2CH_2NHCH_2CH_2$ N HCO), 2.89 (4H, $CONHCH_2$ $CH_2NHCH_2CH_2NHCH_2$ CH_2NHCO), 3.5 (4H, $CONHCH_2CH_2NHCH_2$ CH_2NH CH_2CH_2NHCO), 8.6 (2H, $CONHCH_2$), 7.44 – 9.009 (8H, $NHCOC_5H_4N$). [19] Fig (2).

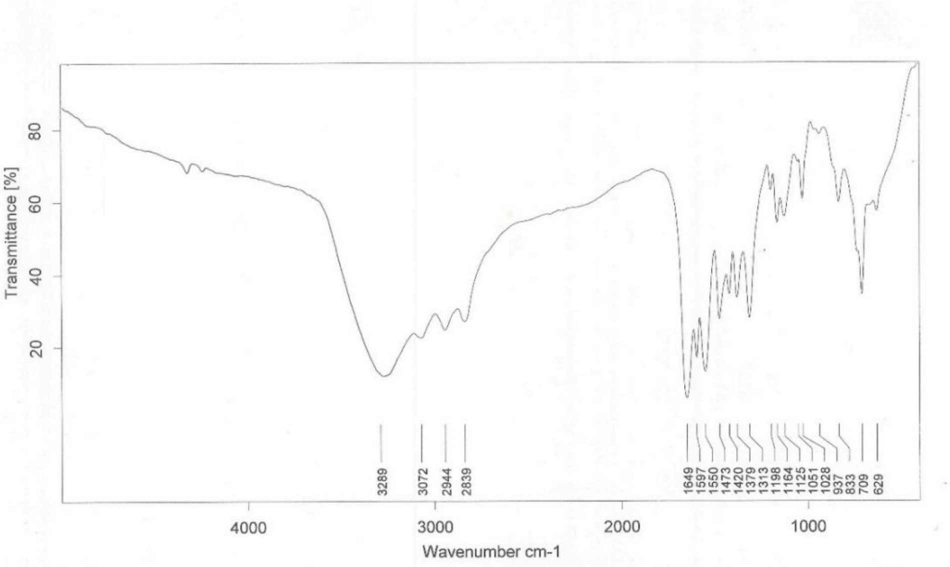
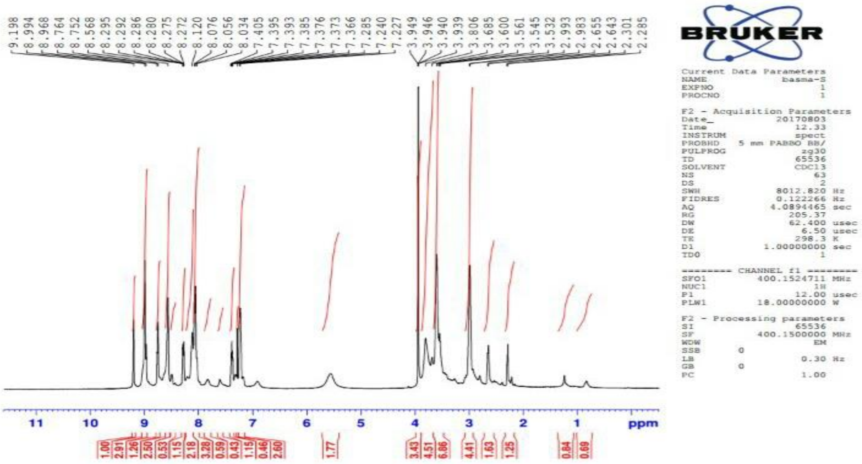


Fig (1): IR spectrum for the synthesized compound.



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PROCNO                    1

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PULPROG                zg30
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NS                       63
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FIDRES         0.122266 Hz
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RG                   205.37
DW               62.400 usec
DE                 6.50 usec
TE                298.3 K
D1           1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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NUC1                     1H
P1                12.00 usec
PLW1        18.00000000 W

F2 - Processing parameters
SI                    65536
SF          400.1500000 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
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Fig (2): ^{1}H-NMR spectrum for the synthesized compound.

3.2. Weight loss measurements

The corrosion behavior of aluminum in 1 M HCl solutions devoid of and containing different concentrations of the five tested compounds was studied using weight loss technique at different time intervals. The rate of corrosion (r) is calculated as g.cm^{-1}.h^{-1}, as following:

$$r = \frac{wt}{At}$$

Where, wt is the weight loss in grams, A is the surface area in square centimeters, of the coupon and t is the time in days.

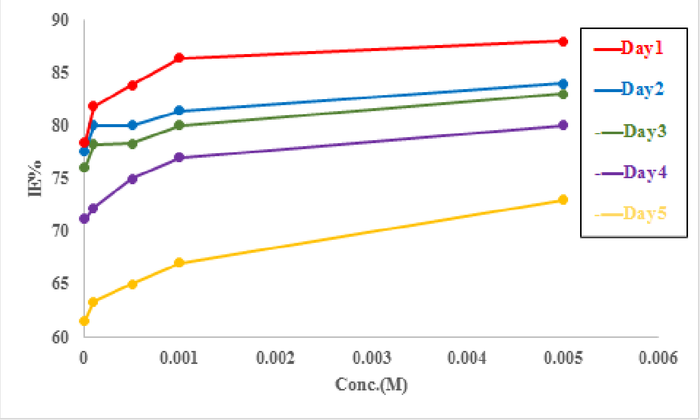

Fig (3): Effect of amide concentration on inhibition efficiency for Carbon Steel corrosion in 1.00 M HCl solution.

Fig (3) represents the effect of amide concentration on inhibition efficiency for Carbon Steel corrosion in 1.00 M HCl solution. The figure shows that, the inhibition efficiency increases as the inhibitor concentration is increased. It is of interesting to note also that the inhibition efficiency increases markedly with increasing concentration up to 10-3 M. Upon increasing the concentration beyond this value, a steady increase in inhibition efficiency is noticed. This implies that a little number of adsorbed molecules can cover a high surface area, which could not be achieved if they are adsorbed vertically. Thus, it could be concluded that the inhibitor molecules adsorb horizontally at the steel surface. Table (1) presents the variation of inhibition efficiency values with both inhibitor concentration and exposed time.

Table (1): Weight loss data of Carbon Steel corrosion in 1.0 M HCl solution.

time	1 day		2 day		3 day		4 day		5 day	
Conc (M)	R×10^5 g/cm^2.day	I.E%	R×10^5 g/cm^2.day	I.E%	R×10^5 g/cm^2.day	I.E%	R×10^5 g/cm^2.day	I.E%	R×10^5 g/cm^2.day	I.E%
Free	100	-	70	-	60	-	55	-	50	-
1x10^{-5}	27	73	22.5	67	21	65	20	63.4	19.2	61.6
1x10^{-4}	20	80	16	77	15.3333	75	14.75	72.2	14.4	71.2
5x10^{-4}	17	83	14	80	12.66667	78.3	12.25	78.2	12	76
1x10^{-3}	16	84	12.5	81.4	11.66667	80	11.25	80	11.2	77.6
5x10^{-3}	12	88	9.5	86.4	9.66667	83.8	10	81	10.8	78.4

3.3. Potentiostatic polarization

Corrosion process is mainly an electrochemical process where the corroded metal acts as anode and dissolved via an anodic reaction. For this metallic dissolution to proceed, a cathodic reaction must take place simultaneously with it at the same rate of the dissolution reaction. The Tafel polarization technique is based on the well-known Tafel equation:

$$\eta = \alpha \pm \beta \ln i$$

where η is the activation polarization of the tested electrode, α is the anodic Tafel constant, β is the cathodic Tafel constant and i is the corrosion current density. The positive sign in the equation stands for the anodic polarization where the negative sign is for the cathodic polarization. The rate of corrosion is determined from the electrochemical techniques as current density.

The corrosion parameters of carbon steel corrosion in free and inhibited 1.00 M HCl solutions obtained from polarization technique are represented in table (2). Investigation of the data in the table reveals that:

i. The corrosion potential does not be affected by the addition of the examined compounds.

ii. The corrosion rate decreases, and the inhibition efficiency increases with increasing additive concentration. Upon increasing the additive concentration in the bulk solution, the number of molecules adsorb on aluminum surface increases leading to an increase in the inhibition efficiency.

iii. Both anodic and cathodic Tafel constants change slightly upon addition of increasing concentrations of the additive. This result indicates that the addition of the tested compounds does not affect the mechanism of aluminum dissolution. Moreover, these findings lead to conclusion that the additive acts as mixed type inhibitor. This type of inhibitors acts by adsorption on both anodic and cathodic sites on the metal surface and thus retards both the anodic and cathodic reactions. This behavior results in decreasing the corrosion rate of the metal.

Table (2): Parameters of carbon steel corrosion in free and inhibited 1.00 M HCl solutions as revealed from polarization technique.

Conc., M	- Ecorr,	βa	-βc	Icorr	IE%
	mV	mV/decade	mV/decade	µA/cm^2	
0	3987.5	111.62	218.72	343	…..
0.00001	458.25	90.442	19.661	8.18	76.2
0.0001	476.95	62.638	10.34	6.34	81.5
0.0005	473.04	85.407	25.699	5.88	82.9
0.001	476.96	54.782	37.168	5.19	84.9
0.005	494.43	65.508	22.254	4.17	87.9

3.4. Effect of temperature

In the temperature range of (303 – 343 ^{0}K), the corrosion rate of carbon steel in 1.00 M HCl was calculated without and with the treatment of 5x10^{-3} M of the amid. Fig (4) show the resulted curves of Tafel polarization. The data drawn from the polarization curves are presented in table (3).

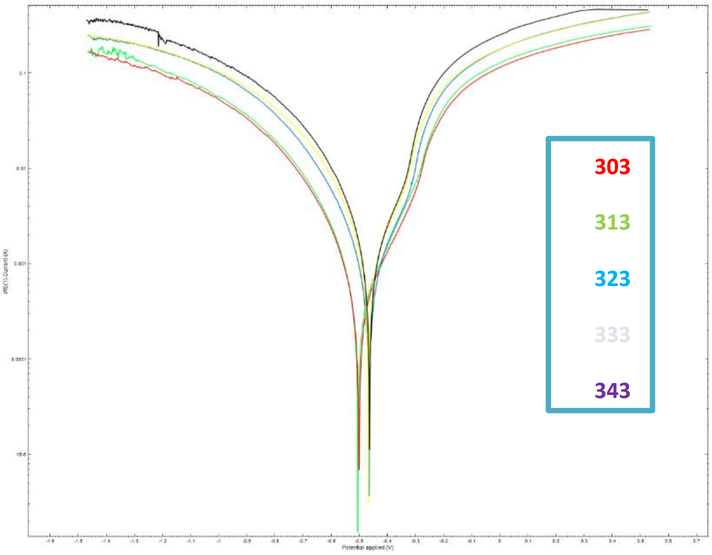

Fig (4): Effect of temperature on the Tafel polarization curves.

Table (3): corrosion parameters of carbon steel in 1.00 M HCl solution in presence of $5x10^{-3}$ M of the synthesized Amide at different temperatures.

	E_{corr}	β_a	β_c	j_{corr} (μA/cm²)	CR (mm/year)	*IE*%	θ
	(V)	(V/dec)	(V/dec)				
303	-0.5251	0.05899	0.22042	570	0.66344	86.8	0.868
313	-0.5078	0.05158	0.01063	790	0.92121	85.7	0.857
323	-0.4683	0.03898	0.02695	1300	1.458	84	0.84
333	-0.469	0.03558	0.02154	1500	1.782	83	0.83
343	-0.471	0.05297	0.055	2300	2.68	82	0.82

3.6. Kinetic parameters

The apparent activation energy (Ea) values for the corrosion of carbon steel in 1.0 M HCl solution in absence and presence of ($5 x 10^{-3}$) M of the synthesized inhibitor were calculated using Arrhenius equation [20]:

$$\ln CR = \ln A - (E_a / RT)$$

Where, CR represents rate of corrosion reaction, A is the Arrhenius constant, R is the gas constant and T is the absolute temperature. Arrhenius plots of ln CR vs. 1/T gave straight lines, as shown graphically in Fig. (5). The slope of the obtained straight lines equal to ($-E_a/R$). The activation energies were calculated and listed in Table (4). The data of the table show that the activation energy (Ea) of the corrosion of carbon steel in 1 M HCl solution in the presence of the amid is higher than that in free acid solution. This result indicates that the amid molecules adsorb on the steel surface forming a barrier prevents mass and charge transfer.

The change in enthalpy and entropy of activation values (ΔH*, ΔS*) were calculated from the transition state theory [21]:

$$\ln (C_R / T) = [\ln(R / N_A h) + (\Delta S^*/ R)] - (\Delta H^* / RT)$$

Where, h is the Plank constant, NA is the Avogadros number, R is the ideal gas constant, ΔH* is the enthalpy of activation and ΔS* is the entropy of activation. Plotting of Ln (Cr/T) versus (1/T), gave straight lines as shown in Fig. (6) With slope of – (ΔH*/R) and the intercept of $\ln(R/N_Ah) + (\Delta S^*/R)$. Values of ΔH* and ΔS* were calculated and listed Table (4).

The positive sign of the enthalpy of activation (ΔH*), reflecting the endothermic nature of the corrosion process and means that the dissolution of carbon steel is difficult in the presence of inhibitor [20]:

The negative sign of entropy of activation (ΔS*), indicates that the activated complex in the rate determining step represents an association rather than dissociation, reflecting that more order take place, going from reactant to activate complex [21]:

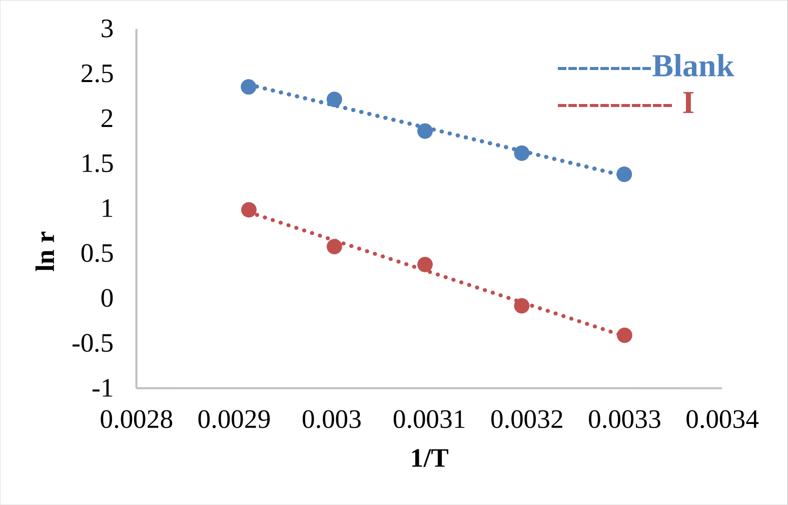

Fig (5): Arrhenius plots for corrosion of steel in free and inhibited HCl solution.

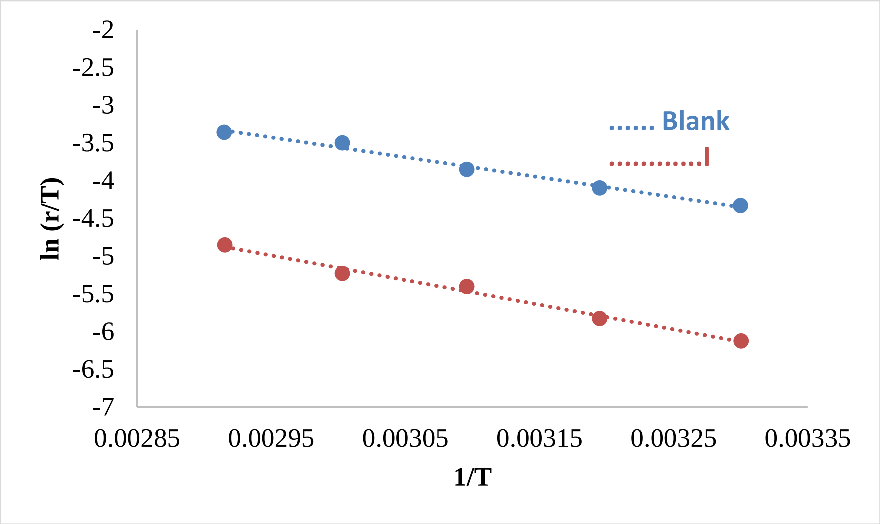

Fig (6): Transition state plots for corrosion of steel in free and inhibited HCl solution.

Table (4): Activation thermodynamic parameters of carbon steel in 1 M HCl in absence and presence of the synthesized IV inhibitor at different temperatures.

	E_a (kJ/mol)	ΔH* (J. mol)	ΔS* (J. mol)
Blank	21.9	21966.09	-161.204
amide	29.8	27279.65	-158.908

3.7. Adsorption isotherm

The degree of surface coverage (θ) for different concentrations of the inhibitor were evaluated from the Potentiodynamic polarization data. The values of surface coverage (θ) of different concentrations of the synthesized amid has been used to find the isotherm of the adsorption process.

Fig. (7) represents the plot of C/θ versus C gave a straight line with correlation coefficient (R^2) equals to 1.0, intercept of ($1/K_{ads}$) and slope closed to 1.0. This indicates that, the adsorption of the amid molecules on the carbon steel surface in 1.0 M HCl solution follows Langmuir's adsorption isotherm, which is represented by the equation [21]:

$$C / \theta = (1 / K_{ads}) + C$$

Where C is the concentration of inhibitor, K_{ads} is the equilibrium constant of the adsorption process and (θ) is the surface coverage.

The free energy of adsorption (ΔG^o_{ads}) was calculated from the following equation:

$$\Delta G^o_{ads} = - RT \ln (55.5\ K_{ads})$$

Where, the value (55.5) is the molar concentration of water.

It was reported that values of ΔG^o_{ads} up to -20 kJ mol^{-1} or lower were consistent with physical adsorption while those about -40 kJ mol^{-1} or higher were consistent with chemisorption [22-24]. The obtained values of ΔG^o_{ads} for the amid is found to be -36.7 kJ/mol, indicates that the adsorption process is spontaneous physical process.

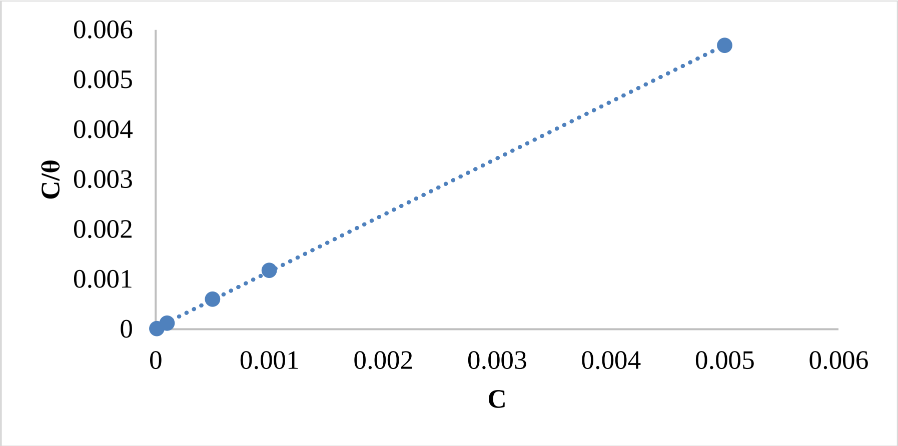

Fig (7): Langmuir isotherm adsorption on the carbon steel surface of different concentration of the synthesized IV inhibitor in 1M HCl solution at room temperatures.

4. Conclusions

1. The synthesized compound in this study were characterized by FTIR and ^{1}H-NMR

2. The synthesized compound acted as good corrosion inhibitors for carbon steel in 1 M HCl.

3. Polarization curves indicated that the prepared compound acted as mixed-type inhibitor for carbon steel in 1 M HCl.

4. Electrochemical and weight loss measurements gave similar results.

5. The corrosion inhibition increased with increasing the inhibitors concentration.

6. The adsorption mechanism of the prepared inhibitor on the carbon steel obeyed the Langmuir adsorption isotherm model.

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