ANTIBACTERIAL DRUG AS A GREEN CORROSION INHIBITOR FOR CARBON STEEL IN AQUEOUS SOLUTIONS

A.A. IDRESS[1]*& Hanan F. EMRAYED[1]

[1]Department of Chemistry, Faculty of Science, Omar Almukhtar University, Albayda, Libya.

*Email: idress.asma@yahoo.com, asma.alsalai@omu.edu.ly

الملخص:

تم دراسة التثبيط و خواص الإدمصاص للامبيسيلين علي تآكل سبيكة الصلب الكربوني بإستخدام طريقة الفقد في الوزن , وجد أن إستخدام الامبيسيلين أدى الي تثبيط تآكل الصلب الكربوني في محلول حامض النيتريك بتركيز 2 مولر وان كفاءة التثبيط تزداد بزيادة تركيز الامبيسيلين و تقل بزيادة درجة الحراره و أن عملية إدمصاص الإمبيسيلين علي سطح السبيكه هي عمليه فيزيائيه طارده للحراره و تلقائيه و تتبع لانجمير أيزوثيرم.

ABSTRACT

Inhibitive and adsorption properties of ampicillin for the corrosion of carbon steel was investigated using chemical **technique** (weight loss method). ampicillin is found to inhibit the corrosion of carbon steel in 2M HNO_3. Inhibition efficiencies of ampicillin increased as its concentration increases but decreased with increase in temperature. The adsorption of the inhibitor on the surface of carbon steel was found to be exothermic, spontaneous and followed the mechanism of physical adsorption. Also Langmuir adsorption isotherm was found to be the best isotherm that described the adsorption characteristics of the inhibitor.

Keywords: corrosion inhibition; carbon steel; ampicillin, HNO_3.

1.INTRODUCTION

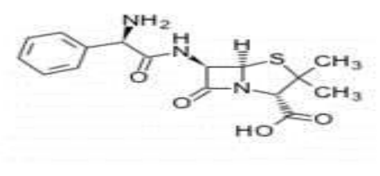
Carbon steel has been widely employed as a construction materials for pipe work in the oil and gas production such as down hole tubular, flow lines and transmission pipelines [1,2]. Therefore, inhibition of corrosion is clearly very important. In the case of carbon steel, the iron will react with hydrogen ions to form

iron ions and hydrogen gas $Fe+2H^{+} \rightarrow Fe^{++}+H_2$ Corrosion cells are created on metal surfaces in contact with an electrolyte because of energy differences between the metal and the electrolyte. Different area on the metal surface could also have different potentials with respect to the electrolyte. The cell contains: 1. Anodic area with a positive charge. The iron is oxidized at the anodic area. 2. Cathodic area with a negative charge. Electrons are present at the cathodic area. These electrons may react with other chemicals in the system. 3.Metallic path that allows electron flow.
4.An electrolyte that covers the iron surface.

A.S. Fouda, and A.A. Idress stated that the inhibiting action of these compound is attributed to their adsorption to the metal/solution interface. It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor group[3]. Like functional groups, aromaticity, electron density at the donor atoms and p-orbital character of donating electrons and also the presence of hetero-atom such as N, O and S, as well as multiple bonds in their molecular structure, are assumed to be active centers of adsorption [4].
But the toxicity of most corrosion inhibitors because they are toxic to living organism and may also poison the earth made us heading for the use of environment-friendly inhibitors [5]. Different types of drugs have been reported in literature to exhibit inhibitive effect on a range of metals in acidic environments. These include sulpha drugs [6], antibacterials [7,8], antifungals [9,10], muscle relaxant [11], among others.

The unique advantage of using natural products for the inhibition of the corrosion of metals is that they are environmentally friendly. Similarly, Eddy NO, and doemelam [12] stated that most heterocyclic drugs are environmentally friendly and can favorably compete with the natural products. However, studies on the use of drugs as corrosion inhibitors are scanty. The scope of the present investigation is to study the corrosion inhibition of carbon steel in 2 M HNO_3, in the presence of different concentrations of ampicillin by weight loss technique at 298 -328K, the thermodynamic functions for the dissolution and adsorption processes were calculated and discussed. The choice of this antibacterial drug was also based on molecular structure considerations, i.e., this is an organic compound with several adsorption centers. Ampicillin is chemically designated as sodium;(2S,5R,6R)-6-[[(2R)-2amino-2phenylacetyl]amino]-3,3-dimethyl-7-oxo-4-thia1azabicyclo[3.2.0]heptane-2 carboxylate. The molecular structure of ampicillin is shown in **Table 1**.

Table 1. Structure of ampicillin

Structure	Mol. formula	Mol.wt.
	$C_{16}H_{19}N_3O_4S$	349.41 g mol^{-1}

2. EXPERIMENTAL

The weight loss measurements were carried out in a100 ml glass beaker placed in a thermostat water bath. The solution volume was 75 mL. The used carbon steel coupons had a rectangular form (length = 2 cm, width = 2 cm, thickness = 0. 3 cm). Prior to all measurements, the coupons were first polished successively with metallographic emery paper of increasing fineness up to 1200 grits. The electrode was then washed with doubly distilled water, degreased with acetone, washed using doubly distilled water again and finally, dried with tissue paper at room temperature. The coupons were weighed and suspended in 75 ml of 2.0 M HNO_3 solution containing ampicillin at the desired concentrations for 3 h at (25-55 °C). At the end of the tests, the coupons were taken out, washed with distilled water, degreased with ethanol, washed again with distilled water, dried and then weighed using an analytic balance (precision: ±0.1 mg)

The inhibition efficiency (% IE) over the exposure time period were calculated according to the following equation:

$$(1)\%\, IE = \theta \times 100 = \left(1 - \frac{W_{(inh)}}{W_{(free)}}\right) \times 100$$

where, θ surface coverage, $W_{(free)}$ and $W_{(inh)}$ are the weight loss in the absence and presence of inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration

The variation of carbon steel weight loss (g) in the presence of varying concentration ($2\times10^{-6} – 1\times10^{-5}$ M) of ampicillin in 2 M HNO_3 for 3.0 h at 25 °C were collected in **Table 3.** and were plotted in **Figure 2.** It was observed that ampicillin inhibits the corrosion of carbon steel in 2M HNO_3 solution at all concentrations used in study, maximum inhibition efficiency was shown at $1x10^{-5}$M concentration of the inhibitor in 2M HNO_3 at 25°C. it is evident from Table 2. that the corrosion rate is decreased on the addition of ampicillin.

Table 2. Corrosion rate (C.R.) in (mg cm^{-2} min^{-1}) and inhibition efficiency data obtained from weight loss measurements for carbon steel in 2 M HNO_3 solutions without and with various concentrations of ampicillin at 25 ± 1°C.

Conc.,M	C.R., mg cm^{-2} min^{-1}	θ	% IE
1 M HNO_3	2.68	-	-
$2x10^{-6}$M	0.80	0.700	70.0
$4x10^{-6}$M	0.56	0.791	79.1
$6x10^{-6}$M	0.39	0.854	85.4
$8x10^{-6}$M	0.35	0.869	86.9

$1x10^{-5}M$	0.19	0.929	92.9

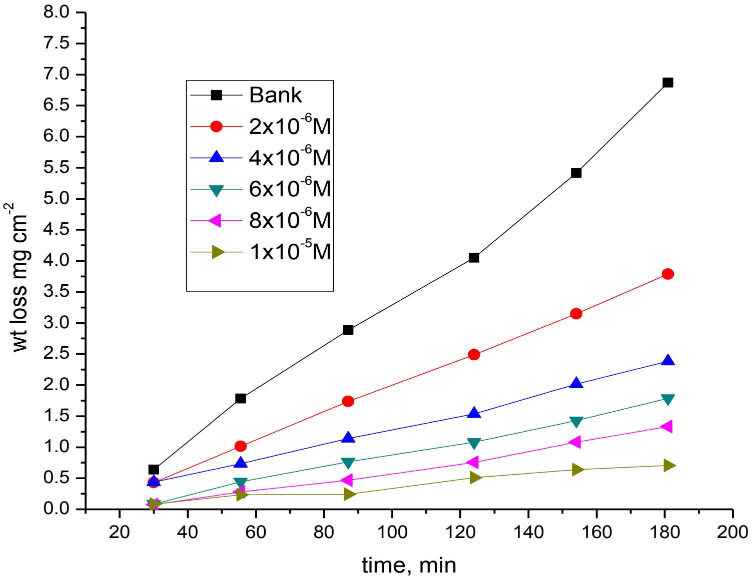


Figure 1. Weight loss-time curves of carbon steel in 2 M HNO_3 in the absence and presence of different concentrations of ampicillin at 25°C.

3.2. Effect of temperature

The effect of temperature, in the range of 25–55 °C with an increment of 10°C on both the corrosion rate and the inhibition efficiency of ampicillin in each of 2M HNO_3, was studied by weight loss measurements and was given in **Table 3.** From **Figure 2.** ; we can see that increasing the temperature leads to an increase in the corrosion rate of carbon steel both in free acid and inhibited acid solution and a decrease in the inhibition efficiency of ampicillin which suggested that corrosion inhibition of carbon steel by the investigated drug caused by the adsorption of inhibitor molecule while higher temperatures caused the desorption of the investigated drug from the carbon steel surface [13].

The apparent activation energy (Ea*), the enthalpy of activation (ΔH*) and the entropy of activation (ΔS*) for the corrosion of carbon steel in 2 M HNO_3 solution in the absence and presence of different concentrations of ampicillin were calculated from Arrhenius-type equation[14] :

$$Rate(k) = A\, e^{\frac{-E_a^*}{RT}} \quad (2)$$

and transition-state equation[15]:

$$Rate(k) = \frac{RT}{Nh}\, e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \quad (3)$$

where (A) is the frequency factor, (h) is the Planck's constant, (N) is Avogadro's number and (R) is the universal gas constant.

Table 3. Data of weight loss measurements for carbon steel in 2 M HNO_3 solution in the absence and presence of different concentrations of ampicillin at 25–55 ±1°C.

Conc.	Temp., °C	C.R., mg cm^2min^{-1}	θ	% IE
$2x10^{-6}$M	25	2.13	0.205	20.5
	35	2.85	0.109	10.9
	45	3.81	0.089	8.9
	55	16.63	0.054	5.4
$4x10^{-6}$M	25	1.26	0.726	72.6
	35	2.15	0.529	52.9
	45	2.97	0.328	32.8
	55	13.63	0.225	22.5
$6x10^{-6}$M	25	0.48	0.819	81.9
	35	1.91	0.709	70.9
	45	9.1	0.543	54.3
	55	0.34	0.482	48.2
$8x10^{-6}$M	25	0.53	0.873	87.3
	35	1.18	0.834	83.4
	45	5.82	0.718	71.8
	55	0.464	0.669	66.9
$1x10^{-5}$M	25	0.072	0.929	92.9
	35	0.059	0.916	91.6
	45	1200.	0.847	84.7
	55	0.010	0.817	81.7

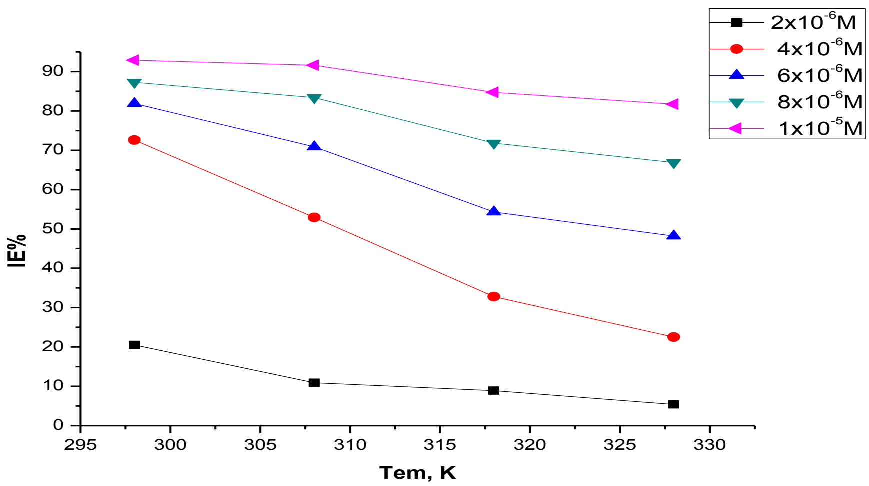


Figure 2. Variation of inhibition efficiency (at $2x10^{-6}$ M - $4x10^{-6}$ M -$6x10^{-6}$M-$8X10^{-6}$M-$1X10^{-5}$M ampicillin) with different temperatures in 2 M HNO_3.

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Kinetic parameters obtained from plots of log Rate vs. (1/T)[**Figure 3.**] and log (Rate/T) vs. (1/T) [**Figure 4.**] are given in Table 5. Inspection of **Table 4.** shows that higher values were obtained for (Ea*) and (ΔH*) in the presence of inhibitor indicating the higher protection efficiency observed for this inhibitor. There is also a parallism between increases in inhibition efficiency and increases in (Ea*) and (ΔH*) values. These results indicate that this tested compound acted as inhibitors through increasing activation energy of carbon steel dissolution by making a barrier to mass and charge transfer by their adsorption on carbon steel surface. The increase in the activation enthalpy (ΔH*) in the presence of the inhibitors implies that the addition of the inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. Also, the entropy ΔS* widely decreases with the content of the inhibitor. This means the formation of an ordered stable layer of inhibitor on carbon steel surface [16].

Table 4. Effect of concentration of ampicillin on the activation energy of carbon steel dissolution in 1 M HNO_3.

Conc. M	**Activation parameters**		
	***Ea kJ mol $^{-1}$**	***ΔH kJ mol $^{-1}$**	***ΔS J mol^{-1} K^{-1}**
2 M HNO_3	36.22	38.66	-8.97
$2x10^{-6}$M	68.82	71.52	-9.20
$4x10^{-6}$M	72.21	85.44	-10.55
$6x10^{-6}$M	83.38	87.34	-13.13
$8x10^{-6}$M	99.12	91.96	-16.93
$1x10^{-5}$M	112.22	99.87	-38.46

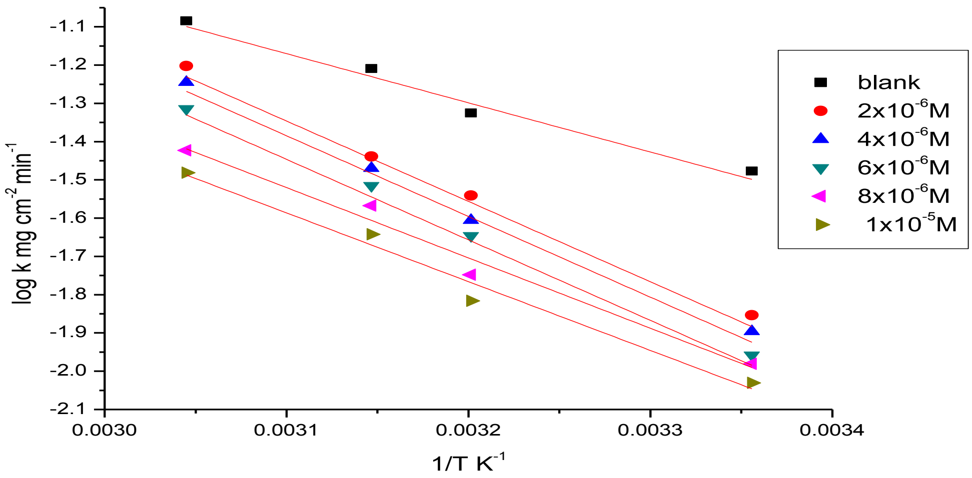

Figure 3. log corrosion rate vs 1/T curves for carbon steel dissolution in 2M HNO_3 in absence and presence of different concentrations of ampicillin.

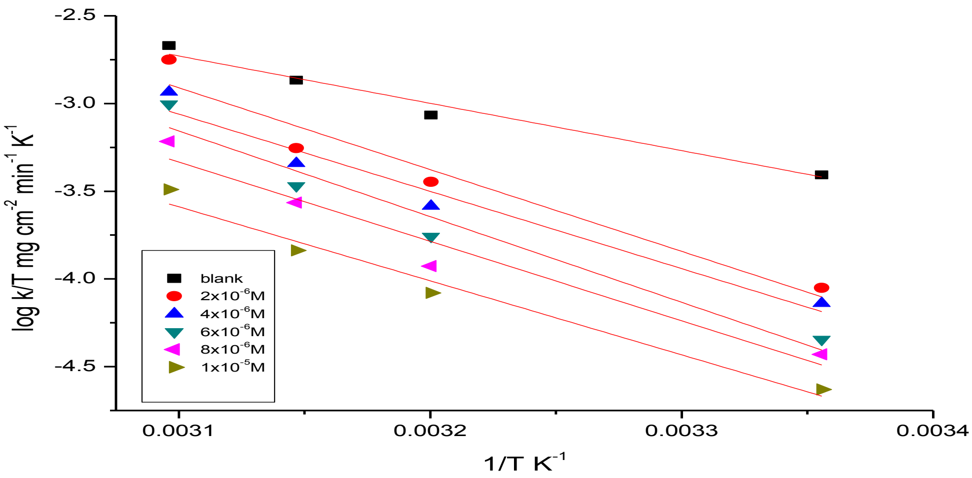

Figure 4. log corrosion rate/T vs 1/T curves for carbon steel dissolution in 2 M HNO_3 in absence and presence of different concentrations of ampicillin.

3.3. Adsorption isotherm behavior

Organic molecules like inhibitors molecules inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process should be considered as a single substitutional process in which an inhibitor molecule, I, in the aqueous phase substitutes an "x" number of water molecules adsorbed on the metal surface:

$$I_{(aq)}+xH_2O_{(sur)} \rightarrow I_{(sur)} + xH_2O_{(aq)} \qquad 4)$$

where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface. When the equilibrium of the process described in Eq. (4) is reached, it is possible to obtain by different expressions of the adsorption isotherm plots [17]. All adsorption expressions include the equilibrium constant of the adsorption process, K_{ads}, which is related to the standard free energy of adsorption ($\Delta G^o_{ads.}$) by [18-20]:

$$K_{ads}=1/55.5\exp-\Delta G^o_{ads}/ RT \qquad (5)$$

where R is the universal gas constant and T is the absolute temperature where 55.5 is the concentration of water in bulk of the solution in mol/L. A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experiment data of the present work. **Langmuir adsorption isotherm was found to be the best isotherm that described the adsorption characteristics of the**

inhibitor. The simplest equation is that due to Langmuir and is given by the general equation:

$$C/\theta = 1/K_{ads} + C \qquad (6)$$

where, C is the inhibitor concentration in the bulk of the solution, θ is the surface coverage and K_{ads} = 1/ intercept . The surface coverage, i.e., the fraction of the surface covered by the inhibitor molecules. **Figure 5.** shows the plot of θ /1- θ vs. C for different concentrations of investigated compound. This plots gives straight line with slope very close to unity. The regression (R^2) is more than 0.9. This means that there is no interaction between the adsorbed species on the electrode surface [3]. The adsorption parameters from Langmuir isotherm are estimated and listed in **Table 5.** The obtained data can be illustrated as follows:

1-The experimental data give good curves fitting for the applied adsorption isotherm as the correlation coefficients (R^2) were in the range 0.978-0.989.

2- K_{ads} value decreases with the increase of temperature from 25 to 55 °C.

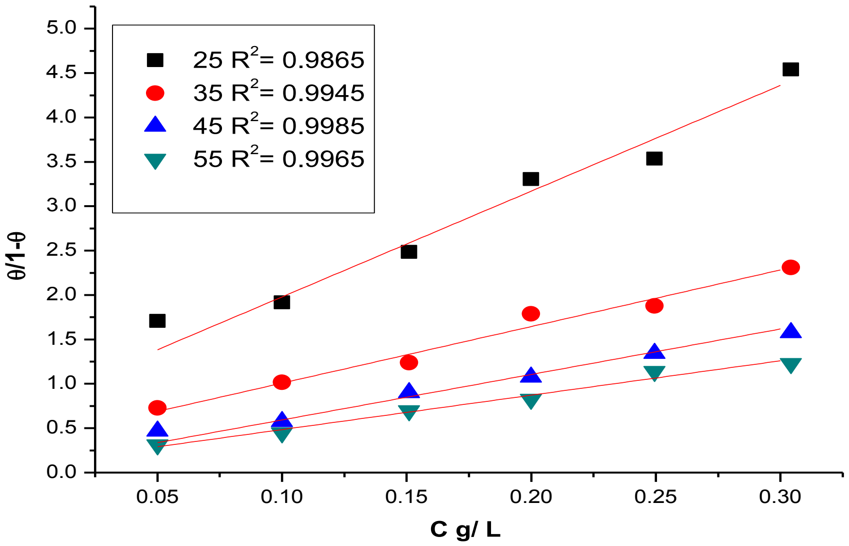

Figure 5. Langmuir adsorption isotherm of ampicillin on carbon steel surface in 2 M HNO_3 at different temperatures.

Table 5. Adsorption parameters for ampicillin in 2 M HNO_3 from Langmuir adsorption isotherm at different temperatures.

Temperature, °C	Adsorption Parameter	
	K_{ads} M^{-1}	R^2
25	29740.00	0.986
35	28262.36	0.994
45	27913.00	0.998
55	27910.74	0.996

3.1.3. Thermodynamic adsorption parameters

The well known thermodynamic adsorption parameters are the free energy of adsorption (ΔG°_{ads}), the heat of adsorption (ΔH°_{ads}) and the entropy of adsorption (ΔS°_{ads}). These quantities can be calculated by various mathematical methods

depending on the estimated values of K_{ads}. From adsorption isotherm, at different temperatures as follows:
The ΔG°_{ads} values at all studied temperatures can be calculated from the equation (7):

$$K = \frac{1}{55.5} e^{\frac{-\Delta G^{\circ}_{ads}}{RT}} \quad (7)$$

The heat of adsorption (ΔH°_{ads}) could be calculated according to the Van't Hoff equation [3]

$$\log K_{ads} = (- \Delta H^{\circ}_{ads} / 2.303RT) + \text{constant} \quad (8)$$

In order to calculate heat of adsorption (ΔH°_{ads}), *log* K_{ads} was plotted against *1/T* as shown in **Figure 6.** The straight lines were obtained with slope equal to ($-\Delta H^{\circ}_{ads}/R$). Then in accordance with the basic equation [21]:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (9)$$

By introducing the obtained ΔG°_{ads} and ΔH°_{ads} values in equation (9), the entropy of adsorption (ΔS°_{ads}) values were calculated at all studied temperatures. All estimated thermodynamic adsorption parameters for the studied compound on carbon steel from 2 M HNO_3 solution were listed in **Table 6.** . Inspection of the obtained data, it was found that:
1- The negative values of ΔG°_{ads} reflect that the adsorption of studied the investigate compounds on carbon steel surface from 2 M HNO_3 solution is spontaneous process [22-24].
2- ΔG°_{ads} values increase with an increase of temperature which indicates the occurrence of exothermic process at which adsorption was unfavorable with increasing reaction temperature as the result of the inhibitor desorption from the carbon steel surface [25].
3- It is usually accepted that the value of ΔG°_{ads} around -20 kJ mol^{-1} or lower indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution while those around -40 kJ mol^{-1} or higher involve charge sharing or charge transfer between the metal surface and organic molecules [26].
4- The negative sign of ΔH°_{ads} reveals that the adsorption of inhibitor molecules is an exothermic process. Generally, an exothermic adsorption process [27]. Generally, enthalpy values up to 41.9 kJ mo^{l-1} are related to the electrostatic interactions between charged molecules and charged metal (physisorption) while those around 100 kJ mo^{l-1} or higher are attributed to chemisorption. The unshared electron pairs in investigated molecules may interact with d-orbitals of α-brass to provide a protective chemisorbed film [28]. In the case of investigated compound, the absolute values of enthalpy are relatively low, approaching those typical of physisorption. The values of ΔS°_{ads} in the presence of investigate compound are large and negative that is accompanied with exothermic adsorption process [29].

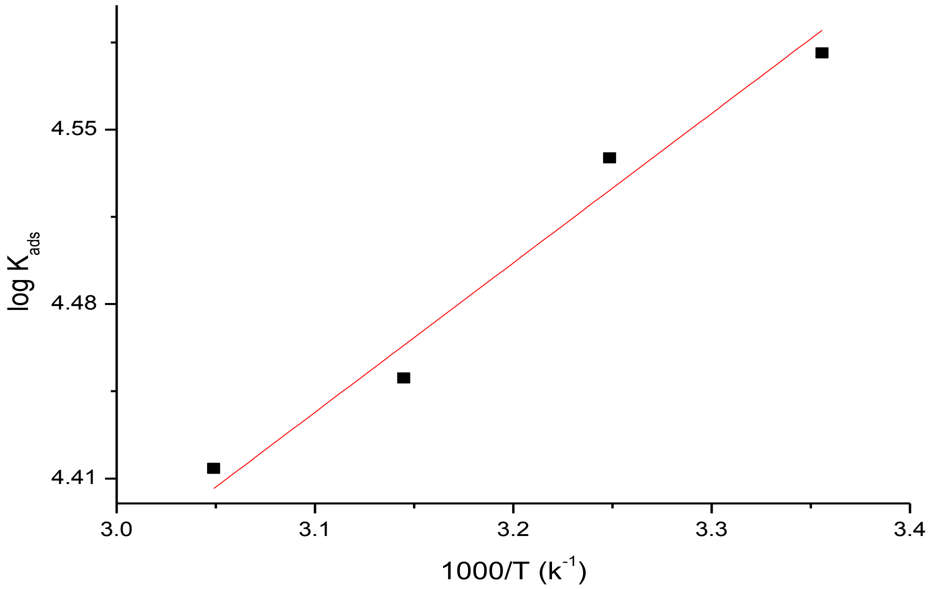

Figure 6. (log k_{ads}) vs. (1 / T) for the corrosion of carbon steel in 2 M HNO_3 in the presence of ampicillin.

Table 6. Thermodynamic parameters for the adsorption of ampicillin on carbon steel surface in 2 M HNO_3 at different temperatures.

Temp,^{O}C	$\Delta G°_{ads}$, kJmol^{-1}	$\Delta H°_{ads}$, kJmol^{-1}	$\Delta S°_{ads}$, Jmol^{-1}
25	-19.22	-35.37	-267.54
35	-17.05		-232.44
45	-15.44		-212.06
55	-14.11		-201.88

4. CONCLUSIONS

From the overall experimental results the following conclusions can be deduced the main conclusions are as follows:

1- ampicillin shows good inhibitive action against the corrosion of carbon steel in 2 M HNO_3.

2- The value of inhibition efficiency increases with increasing the inhibitor concentration and decreases with increasing of the temperature.

3- The adsorption of ampicillin on carbon steel is physical adsorption and obeys Langmuir adsorption isotherm.

4- The negative values of the free energy of adsorption and adsorption heat are indicate that the process was spontaneous and exothermic.

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