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Adsorption Mechanism for Corrosion Inhibition of Carbon Steel on Hcl Solution by Ampicillin Sodium Salt

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ADSORPTIONMECHANISMFORCORROSIONINHIBITIONOFCARBONSTEELONHCLSOLUTIONBYAMPICILLINSODIUMSALT

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I. Introduction

Carbon steel, the most widely used engineering material, accounts for approximately acids are widely used by different industries in various technological processes. In the same time, there is a big problem come from corrosion phenomena especially when we are deal with acid solutions, they are extensively used in a variety of industrial process such as oil acidification, acid pickling and acid cleaning. [1-3]

The protection of metals against the corroding action is accomplished by adding chemical substances of small concentration to environment; these chemicals are called "Inhibitors". So inhibitors are chemical compounds that deposit on exposed metal surfaces from the corrosive environment. The inhibitor may form a uniform film, which like a coating, acts as a physical barrier. Organic compounds which containing sulfur, phosphorus; oxygen nitrogen and aromatic rings are most effective and efficient inhibitors for the metals in acidic medium due to their molecular structure. [4-7]

Several reports have documented the use of many pharmaceuticalscompounds, such as thiophene derivatives [8], methocarbamol [9], penicillin G [10], sulfacetamide(an antibacterial drug) [11], nizoral[12], Cefixime.[13]

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In the present work it was examined the corrosion inhibition and adsorption mechanism for carbon steel in 1M HCl solution by use ampicillin sodium salt and study the interaction of inhibitor concentration (100,200,300,400 and 500 ppm) with temperature effect (303,313,and323 K).

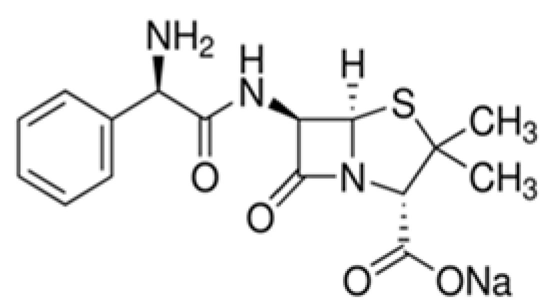
II. Experimental Work

a) Materials

Test were performed on a freshly prepared sheet of carbon steel, Specimens were mechanically cut into (3.0 cm× 3.0 cm × 0.2 cm) dimensions for mass loss tests and 5-mm diameter electrode embedded in polyester for polarization curves tests, then abraded with ambry paper abrasive 400 grit, washed in absolute ethanol and acetone, dried in room temperature and stored in a moisture free desiccator before their use in corrosion studies .

b) Inhibitor

Ampicillin Sodium Salt was used with different concentration (0,100,200,300,400) ppm, as inhibitor, figure -1, show the chemical formula and structure.



Ampicillin Sodium salt

Chemical formula ($C_{16}H_{18}N_3O_4SNa$)

Molecular weight 371.4

Figure 1 : chemical formula and chemical structure for Ampicillin sodium salt

c) Solution

The aggressive solutions, 1 M HCl were prepared by dilution of analytical grade 98% HCl with distilled water.

d) Equipment

Glass equipment (Beaker, Flask, pipet) with different size , water bath (Thermolab Industries – Model H103 – 10 liter capacity – Temp. range 30-90 ^{o} C) , digital balance (Sartorius –Model TE214S with accuracy d=0.1 mg) , desiccator , multi-meter (UNi-T UT804), power supply (ZHAOXIN RXN3010D) , resistance (DECADE RESISTANCE BOX) , Calomel reference electrode , graphite electrode.

e) Gravimetric Measurements

The gravimetric method (weight loss) is probably the most widely used method of inhibition assessment. Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 200 mL test solution at (303 ,313 and 323) K maintained in a thermo stated water bath. The carbon steel coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 1hr. interval, washed thoroughly in 20% NaOH brush, rinsed severally in deionized water, cleaned, dried in, and re-weighed. The weight loss, in grammars, was taken as the difference in the weight of the carbon steel coupons before and after immersion in different test solutions. Then the tests were repeated at different temperatures. The corrosion rate calculated in (mpy).

f) Polarization Measurements

Electrochemical polarization tests were carried out by using three-electrode cell. The specimen was exposed to the solution after it was prepared by polished on a fine grade of ambry paper up to 400 grit and followed by washing with distilled water and finally dried. The electrochemical cell consists to carbon steel as working electrode (WE), a saturated calomel electrode (RE) and graphite as auxiliary electrode (AE), the specimen (WE) was immersed in test solution 500 ml. The circuit was manually composed and the values of current as well as potential were recorded depending on the variable resistance value employed. Figure 2, show the circuit apparatus.

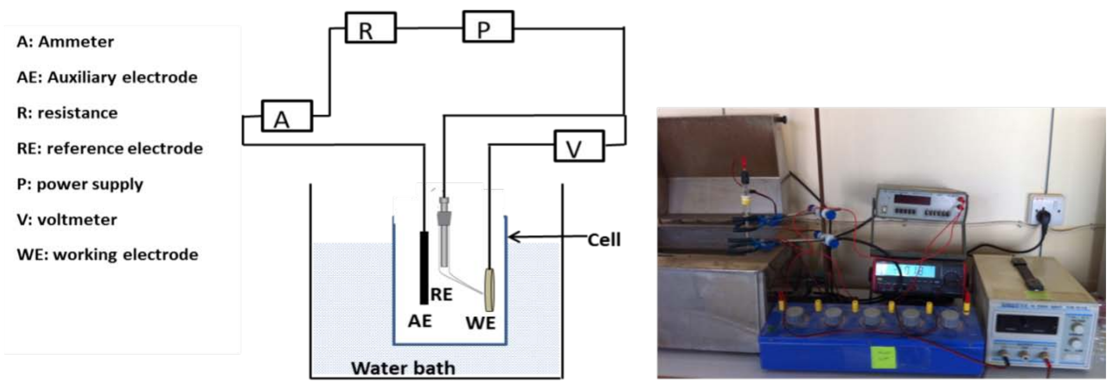


Figure 2 : (left) apparatus of the three electrode cell used in this work (right) show the arrangement for the devices are used in investigation (Corrosion Engineering Lab. Electrochemical Eng. Dept.)

III. Results & Discusion

a) Weight Loss Measurement

Weight loss of carbon steel in 1 M HCl solution was determined in absence and presence (with different concentration) of Ampicillin sodium salt as inhibitor the immersion time was 1 hour with different temperature (303, 313 and 323) K, Table 1 show the results of weight loss investigations, these results were plotted in figure 3.

Table 1 : Variationof corrosion rate in mpy with temperature and inhibitor concentration

Temperature K	Inhibitor concentration M (ppm)	Corrosion rate (mpy) $\times10^{-3}$
303	0 (0)	6.15
	0.000275 (100 ppm)	5.45
	0.000551 (200 ppm)	4.70
	0.000827 (300 ppm)	4.18
	0.001077 (400 ppm)	4.13
313	0 (0)	8.52
	0.000275 (100 ppm)	5.02
	0.000551 (200 ppm)	4.23
	0.000827 (300 ppm)	4.55
	0.001077 (400 ppm)	3.85
323	0 (0)	9.87
	0.000275 (100 ppm)	8.12
	0.000551 (200 ppm)	8.02
	0.000827 (300 ppm)	7.82
	0.001077 (400 ppm)	7.45

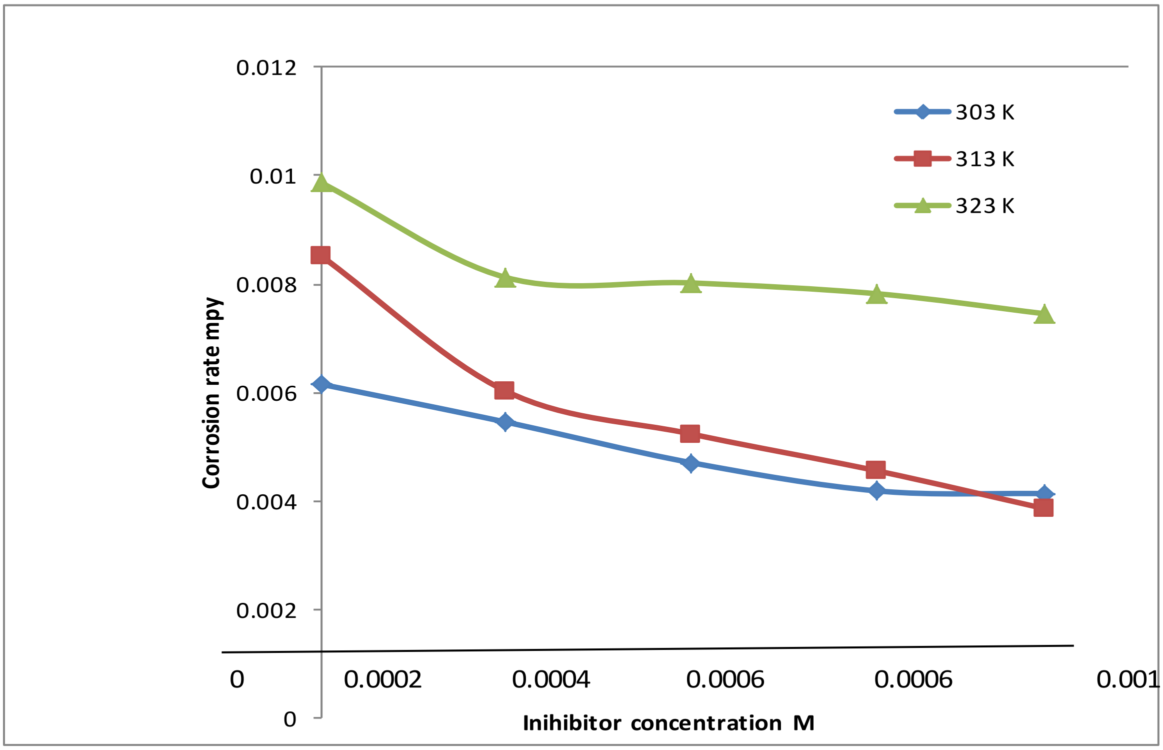


Figure 3 : corrosion rate of carbon steel in 1 M HCl solution with absence and presence of Ampicillin sodium salt by weight loss with immersion time 1 hour at different temperature

b) Electrochemical Measurement

Table 2 shows the galvanostatic polarization curves (potential versus logarithmic current density) at different temperature (303, 313, and 323) K with different inhibitor concentrations (0,100, 200, 300, and 400) ppm the study was carried out on carbon steel electrode in 1 M HCl , the inhibitor efficiencies which were listed in table 2, which calculated according to below equation:

$$\eta\% = \frac{W_u - W_i}{W_u} x100 = \left[1 - \frac{W_i}{W_u}\right] x100. \qquad (1)$$

Where i_{un}, and i_{in} are the corrosion current densities for uninhibited and inhibited condition respectively. The last column in table 2, for surface coverage,

$$\theta = \frac{W_u - W_i}{W_u} = \left[1 - \frac{W_i}{W_u}\right] \qquad (2)$$

Polarization curves were plotted in figures 4, 5 and 6 at 303, 313and 323 K respectively

Table 2 : Corrosion parameters at different condition

Temperature K	Inhibitor concentration M (ppm)	i corr µA/cm2	βc (mV / dec)	βa (mV / dec)	- E_{corr} mV	η%	θ
303	0	318.1	483.5	917.4	430	0	0.00
	0.000275 (100 ppm)	254.5	495.1	674.7	435	20	0.20
	0.000551 (200 ppm)	207.3	665.9	535.6	438	35	0.35
	0.000827 (300 ppm)	169.8	752.4	716.1	450	47	0.47
	0.001077 (400 ppm)	124.6	899.3	985.0	451	61	0.61
313	0	463.2	280.6	181.3	445	0	0.00
	0.000275 (100 ppm)	384.5	283.2	145.1	457	17	0.17
	0.000551 (200 ppm)	319.6	309.2	328.9	466	31	0.31

Global Journal of Researches in Engineering (J) Volume XIII Issue IV Version I Year 2013

	0.000827 (300 ppm)	268.7	309.5	370	471	42	0.42
	0.001077 (400 ppm)	194.5	353.4	302.1	479	58	0.58
323	0	642.3	190.8	305.1	448	0	0.00
	0.000275 (100 ppm)	526.7	221.4	197.6	456	18	0.18
	0.000551 (200 ppm)	456.0	204.8	247.8	459	29	0.29
	0.000827 (300 ppm)	385.4	235.0	343.3	465	40	0.40
	0.001077 (400 ppm)	301.9	267.8	203.7	469	53	0.53

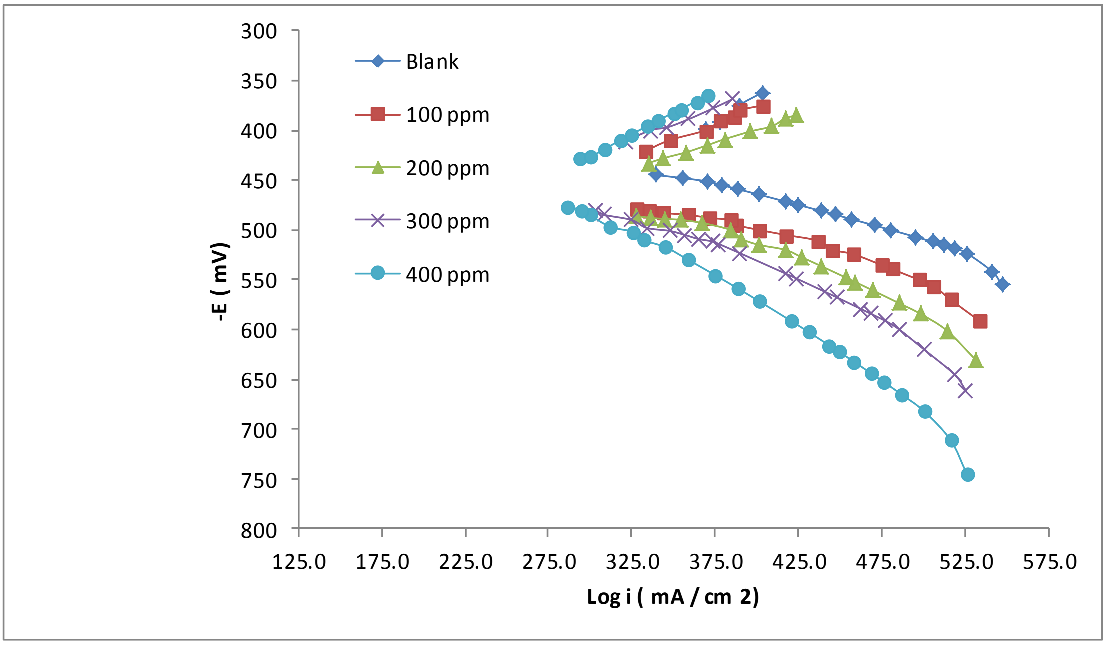


Figure 4 : Polarization curves of carbon steel in 1 M HCl solution which containing different inhibitor concentration at 303 K

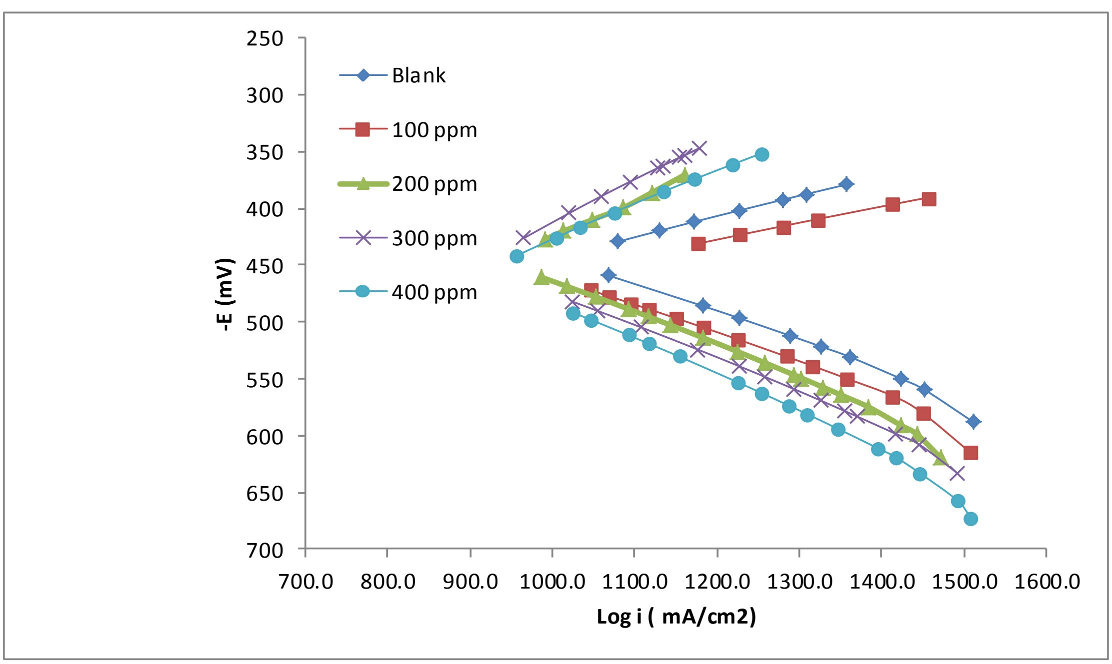


Figure 5 : Polarization curves of carbon steel in 1 M HCl solution which containing different inhibitor concentration at 313 K

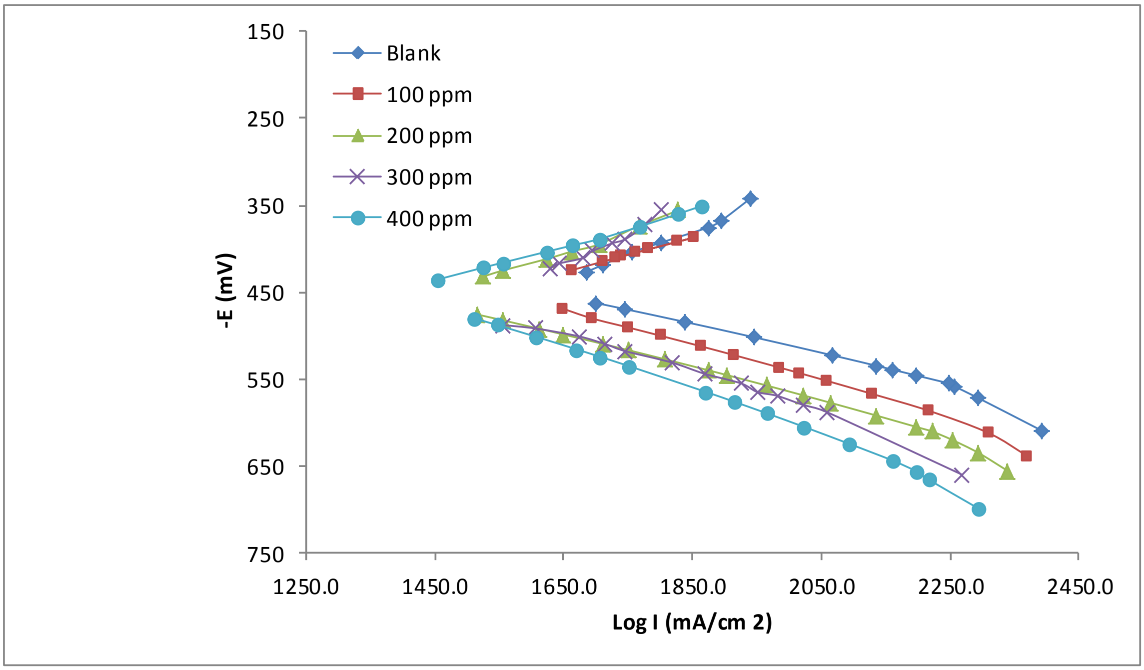


Figure 6 : Polarization curves of carbon steel in 1 M HCl solution which containing different inhibitor concentration at 323 K

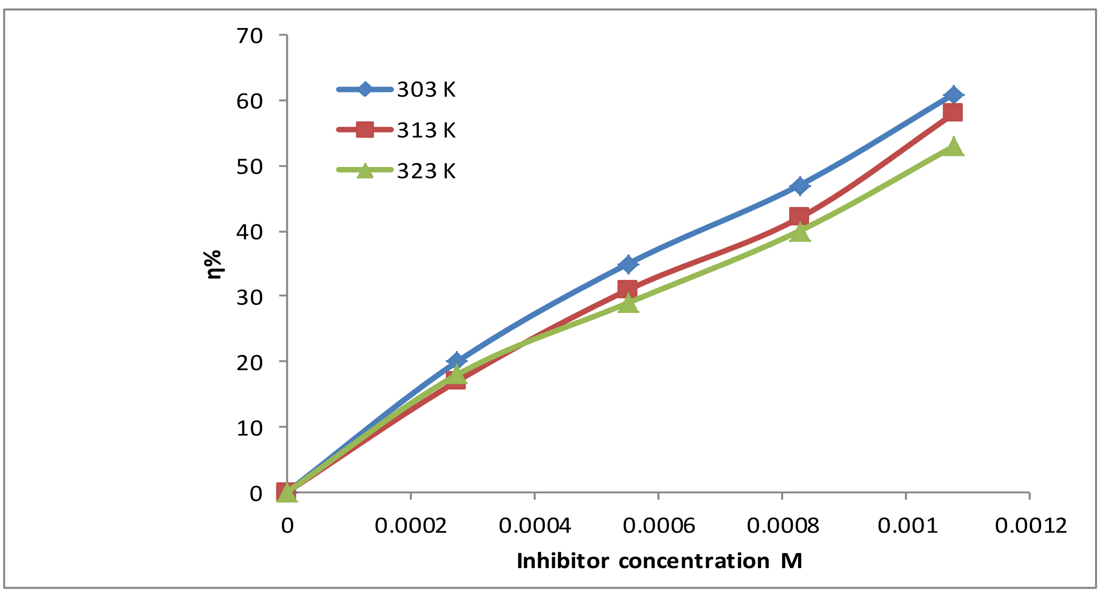


Figure 7 : variation of inhibition efficiency with inhibitor concentration at different temperature (303,313, and 323) K

c) Absorption Isotherms

The adsorption of organic compounds can be described by two mains types of interaction; physical adsorption and chemisorption .they are influenced by the nature of the change of the metal, the chemical structure of inhibitor, pH, the type of electrolyte and temperature. [14]

So adsorption isotherms are very important in determining the mechanism organic electrochemical reaction [15], the most frequently used isotherms are Langmuir, FrumKin, Temkin, Flory-Huggin, and etc. all these isotherms are of general form

$$f(\theta, x)\exp(-2a\theta) = KC$$

Freundlich adsorption isotherm was found to be suitable for the experimental findings; the isotherm is described by equation

$$\theta = K_{ads} c^{n} \qquad (3)$$
$$\log\theta = \log K_{ads} + n\log C$$

Where C is inhibitor concentration, K_{ads} is adsorption equilibrium constant and θ is the surface coverage and *n* is constant, and the adsorption free energy was estimated from the following equation, adsorption equilibrium constant was calculated from plot at figure 8 , the value of them (adsorption equilibrium constant and free energy) were listed in table 3.

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (4)$$
$$\Delta G^{\circ}_{ads} = -RT\ln(55.5\ K_{ads})$$

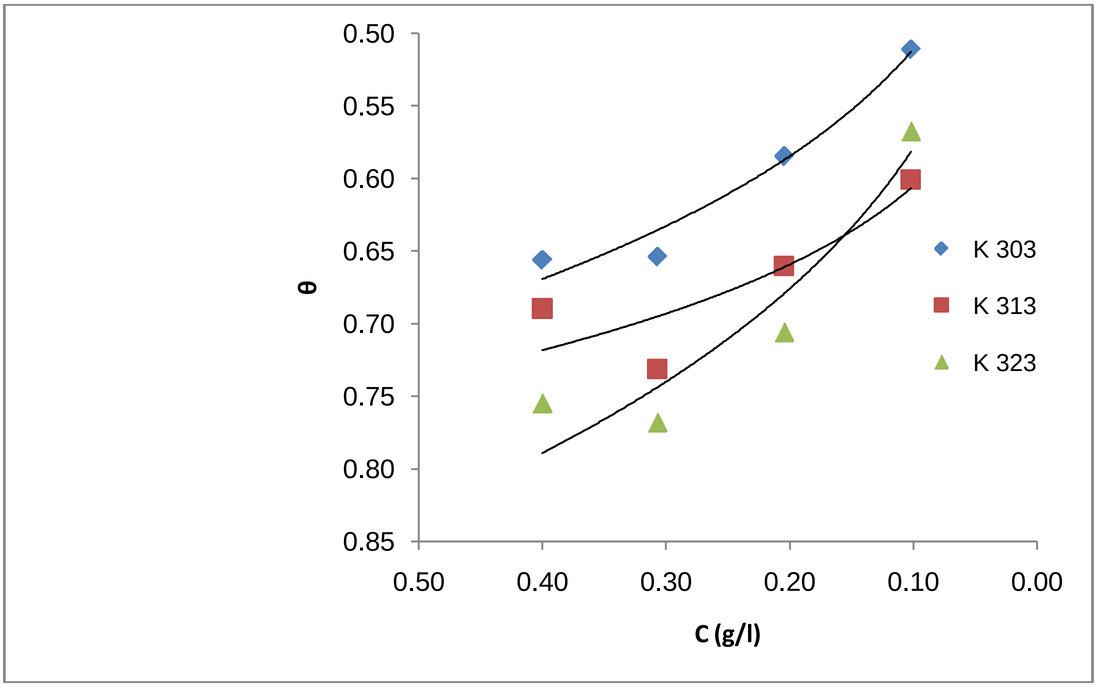


Figure 8 : Freundlich adsorption isotherms for carbon steel in 1 M HCl solution in absence and presence of Ampicillin sodium salt at 303, 313 and 323 K

Table 3 : Inhibitor adsorption constant and free energy of founded by use Freundlich adsorption isotherm for carbon steel in 1 M HCl solution in absence and presnce of Ampicillin sodium salt at 303, 313 and 323 K

Temperature K	K_{ads} adsorption equilibrium	Free energy ΔG_{ads} kJ/mol
303	6.32	-14.76
313	6.37	-15.27
323	9.31	-16.77

d) Effect of Temperature

The influence of temperature on the corrosion behavior of carbon steel in HCl solution with added various inhibitor concentrations can be obtained by estimation of activation energies.

Activation energies were calculated from the Arrhenius plots, when plot logarithmic corrosion current density (log i_{corr}) versus reciprocal absolute temperature, relationship between them can be expressed according to the following equation. This behavior was shown in figure 9

$$\log i_{corr} = \log A - \frac{E}{2.303RT} \qquad (5)$$

Other parameters such as enthalpy (ΔH°) and entropy (ΔS°) of activation of corrosion process may be evaluated from effect of temperature .an alternative formulation of Arrhenius equation called transition state plot is helpful.

$$i_{corr} = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^{\circ}}{R}\right)\exp\left(\frac{-\Delta H^{\circ}}{RT}\right) \qquad (6)$$

Where h is Planck's constant, N Avogadro number and, R is universal gas constant.

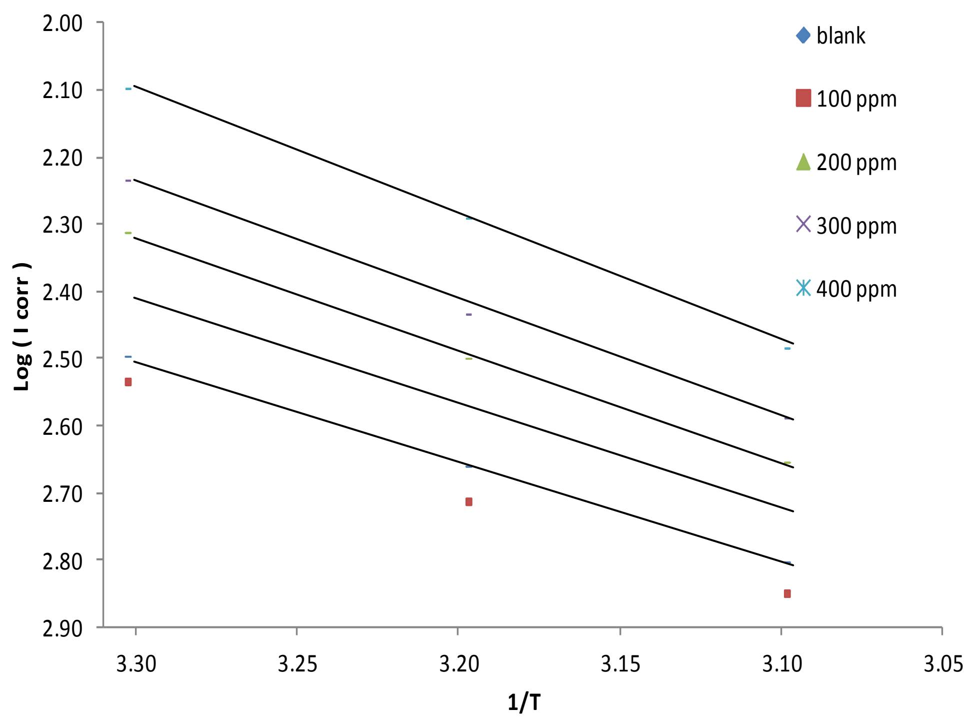


Figure 9 : Arrhenius plot for carbon steel in 1 M HCl solution in absence and presence of Ampicillin sodium salt

Table 4 : Activation and thermodynamics parameters for carbon steel corrosion in 1 M HCl solution in absence and presence of Ampicillin sodium salt

Inhibitor conc. (M) ppm	$E_{act.}$ (kJ/mol)	Enthalpy ΔH° (kJ/mol)	Entropy ΔS° (kJ/mol.K)
0	28.61	11.29	123.25
0.000275 (100 ppm)	29.63	11.74	123.94
0.000551 (200 ppm)	32.10	12.81	126.73
0.000827 (300 ppm)	33.38	12.81	127.86
0.001077 (400 ppm)	36.00	14.81	130.44

It can be seen from the above that; 1- the current density is decreased by the addition of the specified inhibitor concentration and the decrease is proportional to the inhibitor quantity.2- the current density is increased with increasing of temperature.3- the corrosion potential does not altered significantly with both the temperature and the inhibitor quantity.4- all the curves are lying within the activation control region.

The value of thermodynamic parameters for the adsorption of inhibitors can provide information about the mechanism of corrosion inhibition. The endothermic adsorption process (Q >0) is attributed unequivocally to chemisorption), while generally, an exothermic adsorption process (Q< 0) may involve either physisorption or chemisorption or a mixture of both. In general the value of adsorption heat is exothermic (table 3), i.e. as the temperature is increased the inhibition efficiency is expected to be in decreasing order. This can be explained that the effective part of the extract is not available in such density to be in contact with the metal surface and here the physical adsorption is prevailing. As the inhibitor concentration increased the availability of acting parts (the composer of tea) is increased and the reaction is becoming easier and faster. According to this statement, there are two actions of this inhibitor viz. by physorption and chemisorption one.

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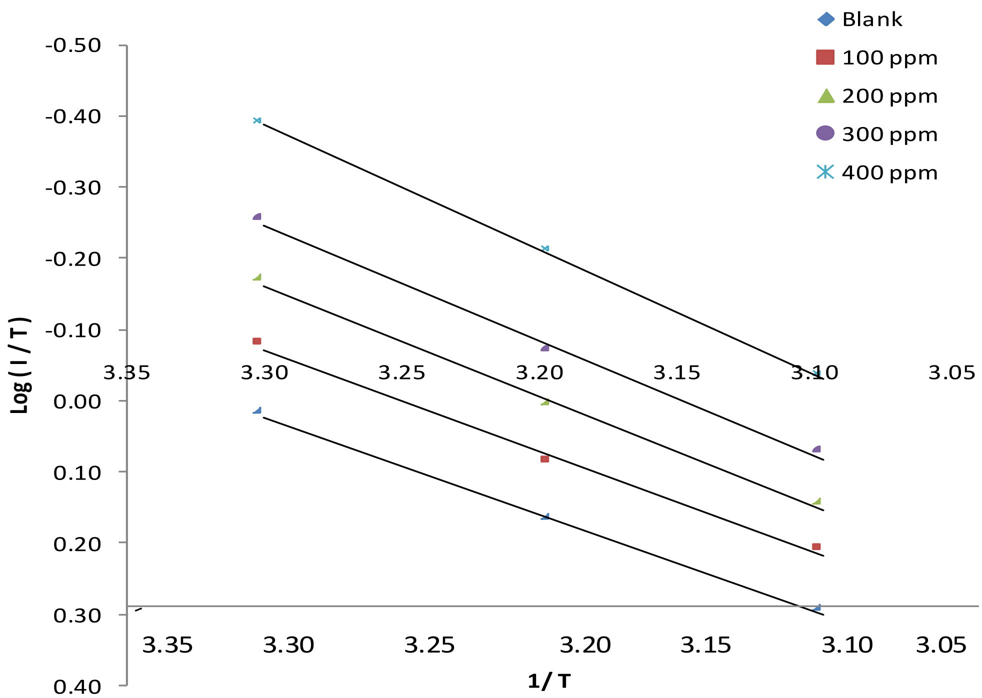

Figure 10 : Transition state plot for carbon steel corrosion in 1M HCl solution in absence and presence of Ampicillin sodium salt

The values of ΔS can be obtained from the plot of log icorr/T as shown in figure 10 and enlisted in table 4 above. These values of entropy suggest that as the quantity of inhibitor increases the order of the reactants to go to the activated complex or as the inhibitor quantity increased the formed film becomes well ordered

IV. Conclusions

- Ampicillin sodium salt as a mixed inhibitor for the corrosion of carbon steel in 1 M HCl solution without affecting the mechanism of hydrogen evolution reaction.
- The inhibition efficiency of Ampicillin sodium salt increases-almost-with temperature and the activation energy decreases in presence of the inhibitor.
- The inhibitor efficiency increased by increasing inhibitor concentration.

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