

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

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Abstract

In this study, the inhibitor effect of ampicillin sodium salt on carbon steel corrosion in 1M of HCl solution was investigated. The experiment was carried in HCl solution different temperature (303,313, and 323) K and by used different inhibitor concentration, the weight loss and polarization curve investigation were done. The activation energy, heat of adsorption and thermodynamic parameters of inhibition effect of Ampicillin sodium salt under investigation on the corrosion process have been calculated at different temperature. It was found the effect of inhibitor was decrease with increasing temperature and Ampicillin sodium salt as a mixed inhibitor for the corrosion of carbon steel. 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.

Index terms— corrosion, corrosion inhibitor, adsorption isotherm.

1 Introduction

Carbon steel, the most widely used engineering material, accounts for approximately 50% of the total steel production. It is 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][2][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][5][6][7] Several reports have documented the use of many pharmaceuticals compounds, such as thiophene derivatives [8], methocarbamol [9], penicillin G [10], sulfacetamide (an antibacterial drug) [11], nizatidine [12], Cefixime. [13] 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, and 323 K).

2 II.

3 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

7 RESULTS & DISCUSION A) WEIGHT LOSS MEASUREMENT

acetone, dried in room temperature and stored in a moisture free desiccator before their use in corrosion studies .

4 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. Glass equipment (Beaker, Flask, pipet) with different size , water bath (Thermolab Industries -Model H103 -10 liter capacity -Temp. range 30-90 ° 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.

5 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).

6 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.

7 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 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:.. $100 \frac{i_{un} - i_{in}}{i_{un}} \times 100 \% = ?$ (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, $\theta = \frac{i_{un} - i_{in}}{i_{un}} = ?$ (2)

Polarization curves were plotted in figures 4, 5 and 6 at 303, 313and 323 K respectively 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. J 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 $K C a \times f = ?$ $2 \exp()$, (? ?

Freundlich adsorption isotherm was found to be suitable for the experimental findings; the isotherm is described by equation $\log \log C n K c K_{ads} n_{ads} + = ?$? (3)

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. 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 $303 . 2 \log \log RTE A i_{corr} ? = (5)$

Other parameters such as enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation of corrosion process may be evaluated from effect of temperature .an alternative formulation of Arrhenius equation called transition state plot is helpful. $303 K 313 K 323 K D D D D) J \exp ? = RT H R S N h RT i_{corr} ? ?$ (6)

Where h is Planck's constant, N Avogadro number and, R is universal gas constant. 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.3the 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 physisorption and chemisorption one. The values of $\Delta S^\ddagger$ can be obtained from the plot of $\log i_{corr}/T$ 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.

8 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.

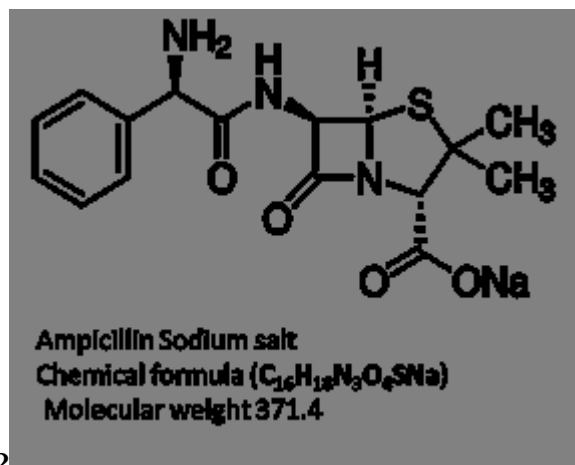
? The inhibitor efficiency increased by increasing inhibitor concentration. ^{1 2}



Figure 1: Figure 1 : 2 Global

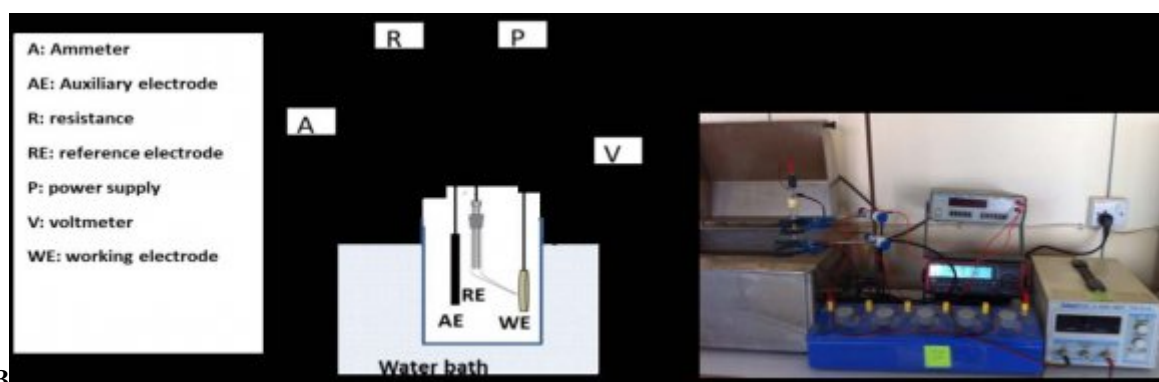
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2

Figure 2: Figure 2 :



3

Figure 3: Figure 3 :

1

			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
temperature and inhibitor concentration			ppm) 0.001077 (400	3.85
	323		0 (0)	9.87
Temperature Inhibitor	Corrosion		0.000275 (100	8.12
	rate			
K	concentration	(mpy)	ppm)	
		$\times 10^{-3}$		
	M (ppm)		0.000551 (200	8.02
303	0 (0)	6.15	ppm)	
	0.000275 (100 ppm)	5.45	0.000827 (300 ppm)	7.82
	0.000551 (200 ppm)	4.70	0.001077 (400 ppm)	7.45

Figure 4: Table 1 :

2

Temperature K	Inhibitor concentration M (ppm)	i corr A/cm ²	η_c (mV / dec)	η_a (mV / dec)	-E corr mV	$\eta\%$	η
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

Figure 5: Table 2 :

3

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		

Figure 6: Table 3 :

4

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

Figure 7: Table 4 :

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