

Methyl Violet Dye as Corrosion Inhibitor for Carbon Steel in Acidic Medium

Hamida Edan Salman*, Maha jassim Manshad

Chemistry Department, College of Education for Pure sciences, University of Kerbala, Iraq.

*Corresponding Author: Hamida Edan Salma

Abstract

The present work involves study the Methyl Violet dye as a corrosion inhibitor with concentrations rang (25- 200) ppm for their influence on carbon steel corrosion in 1M H₂SO₄ at temperature range (303-323) K utilize potentiodynamic polarization technique. Corrosion rates, Corrosion potential, current corrosion, inhibition efficiency, cathodic and anodic Tafel slopes were found. The study also examined influence of concentration and temperature on inhibition efficiency the results manifest that the dye utilized could be good and active inhibitor for carbon steel. Thus, the dwindle in the rate of corrosion is due to the of forming of a protective strata formed on the surface electode that which adsorbed physically and chemically on the surface of carbon steel. Energy values of activation (E_a), enthalpy (ΔH^*), energies of Gibbs (ΔG^*), and activation entropy (ΔS^*), alongside along thermodynamic amounts of corrosion and adsorption provision indicating the dye effect as a good inhibitor. The isotherm langmuir paradigm be obvious shaped well to enhanced the adsorption operation on carbon steel surface in acidic solution.

Introduction

Corrosion phenomenon may be take place because of using acid solutions like sulfuric acid which is more used in several manufacture fields such as for pickling, acid purgation of boilers [1, 3]. So the organic inhibitors are commonly utilized as one of the more effective, workable and less be priced technicality for metal preservation from the influence of acids (acidic corrosion) [4, 5]. In which the inhibitors work to inhibit the corrosion process in acidic media by expulsion the H₂O molecules and form a protective layer [6].

Organic compounds that contain heteroatoms in their structures (like sulfur, oxygen, nitrogen etc), aromatic ring and conjugated diverse bonds (π) these features makes the organic inhibitors have an ability to get adsorption superficially of metals and consequently avoid the metal from corrosion process [7, 9].

Dyes are organic compounds of which about 1 million tonnes are generated annually due to their paramount applications in unlike industries such as weaving, paper, food, cosmetics, leather, chemical and pharmaceutical industries [10, 12]. A number of studies on the utilize of dyes as organic inhibitors for the corrosion operation have also been finished [13]. Anyway, the corrosion operation cannot be stopped but can be retarded because it is a normal process to return the compositional elements of the synthesized alloys into their root [14].

The study aims to study the electrochemical process of corrosion of carbon steel in acidic medium with and without adding (25-200) ppm of dye (methyl violet) as an inhibitor at different temperatures (303-323) K under stable situation. Chemical molecular structure of the inhibitor is shown below [15].



Chemical molecular structure of methyl violet dye

Experimental

Specimens Preparation

A rod of carbon steel has been cut into cylindrical samples with dimensions (25 mm diameter and 3 mm height). Its components compositional are 0.169% C, 0.141% Si, 0.652% Mn, 0.0062% P, 0.018% S, 0.0545% Cr, 0.0039% Mo, 0.0678% Ni, 0.0104% Al, 0.224% Cu and Fe balanced. The carbon steel specimen utilized as a working electrode. Firstly, the samples polished mechanically by several grades of emery papers (from 80 to 3000) grade.

The specimens are then remedied with a micro cloth and polishing paste to be given a mirror-like surface, finally it was washed with distilled water and then absolute ethanol. The sample kept in desiccators to safeguard and prevent them from oxidation by air and wetness.

Corrosive Environment Solutions

The attacker solution 1M H₂SO₄ was prepared through mitigation of analytical degree 98% H₂SO₄ solution with distilled water.

Inhibitor Preparation

The concentrations used for the inhibitor methyl violet dye is in the acid medium (25,50, 100, 150,200) ppm where a certain amount has been weighed to prepare the required concentration of the inhibitor (dye) and these weights are dissolved directly in the acid, then the volume is supplemented with distilled water.

Polarization Measurements

Potentiostatic polarization measures were performed via the three cell electrodes. The satiated calomel electrode Hg / Hg₂Cl₂ was utilize as a reference electrode and the platinum electrode was employed as an auxiliary electrode and working electrode. The carbon steel model was connected to the working electrode through exposed territory of 1 cm². After which the working electrode was inundation in the trial solution for 30 minutes with a time stride of 1 second.

The alteration in the electrode voltage was automatic (± 250 m v) relative to the open circuit potential (OCP) . At a scan rate (0.3 mVs⁻¹). The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were deliberate by Tafel method. The inhibition efficiency (η %) was calculated as in equation (1) [16].

$$\eta (\%) = \frac{I_{corr} - I_{inh}}{I_{corr}} \times 100 \dots\dots\dots (1)$$

Where η (%) is the ratio of the efficiency of inhibition, i_{corr} and i_{inh} is corrosion current density in the absence and presence of inhibitor .

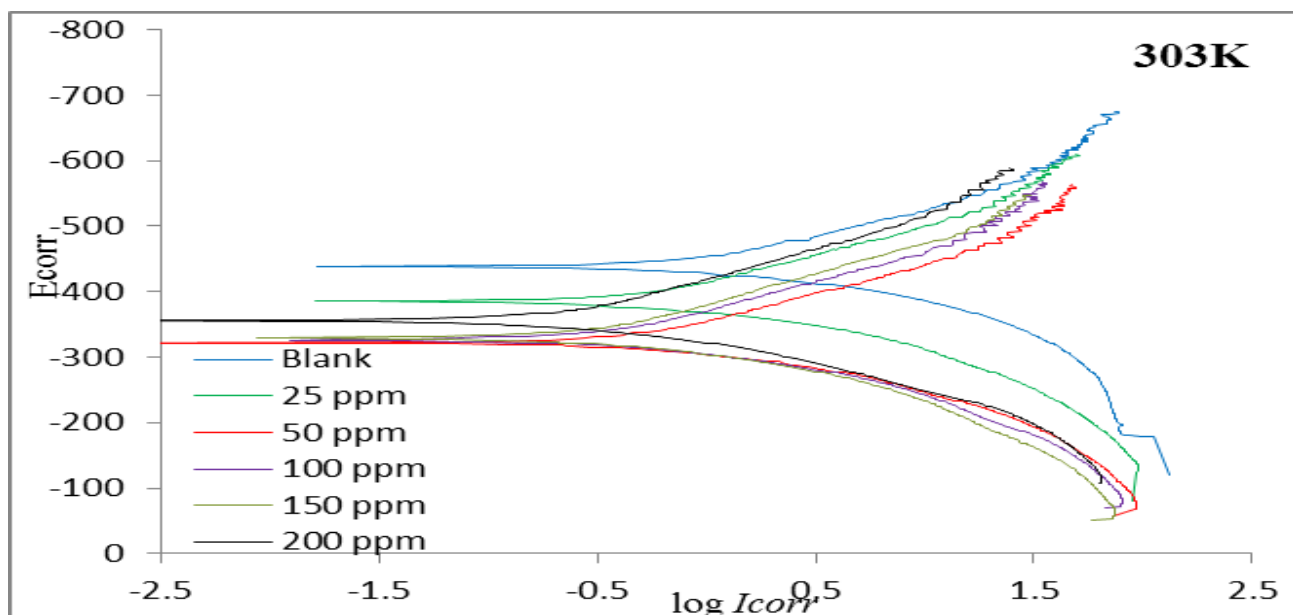
Results and Discussion

Electrochemical Method

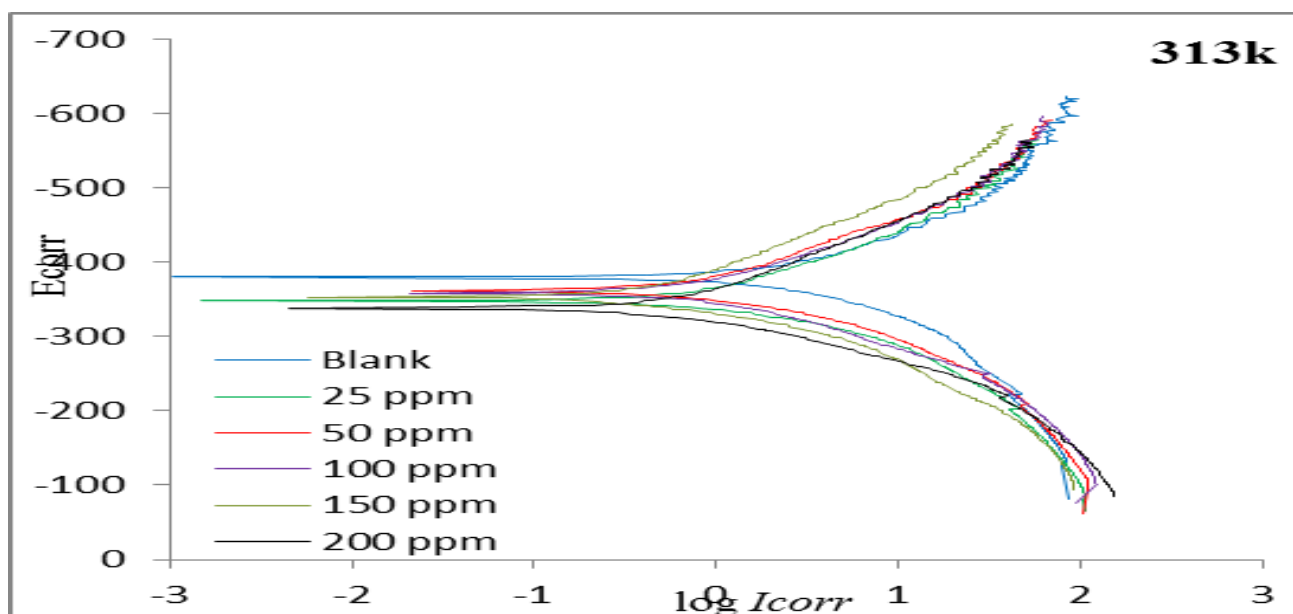
The Figures (1-3) show the polarization curves For the purpose of understanding the influence of the inhibitor on the corrosion of carbon steels in 1M H₂SO₄ solution where potential polarization measurements were made in the existence and absence of various methyl violet dye concentrations (25-200) ppm at several temperatures (303- 323)K Table (1) shows the experimental results measured included corrosion potential

(E_{corr}), corrosion current density (i_{corr}), anode and cathode Tafel slopes (β_a , β_c), inhibition efficiency (η %) and surface coverage (θ) When the methyl violet dye added, there was a decrease in the corrosion current intensities of the carbon steel by increasing the concentration at constant temperatures.

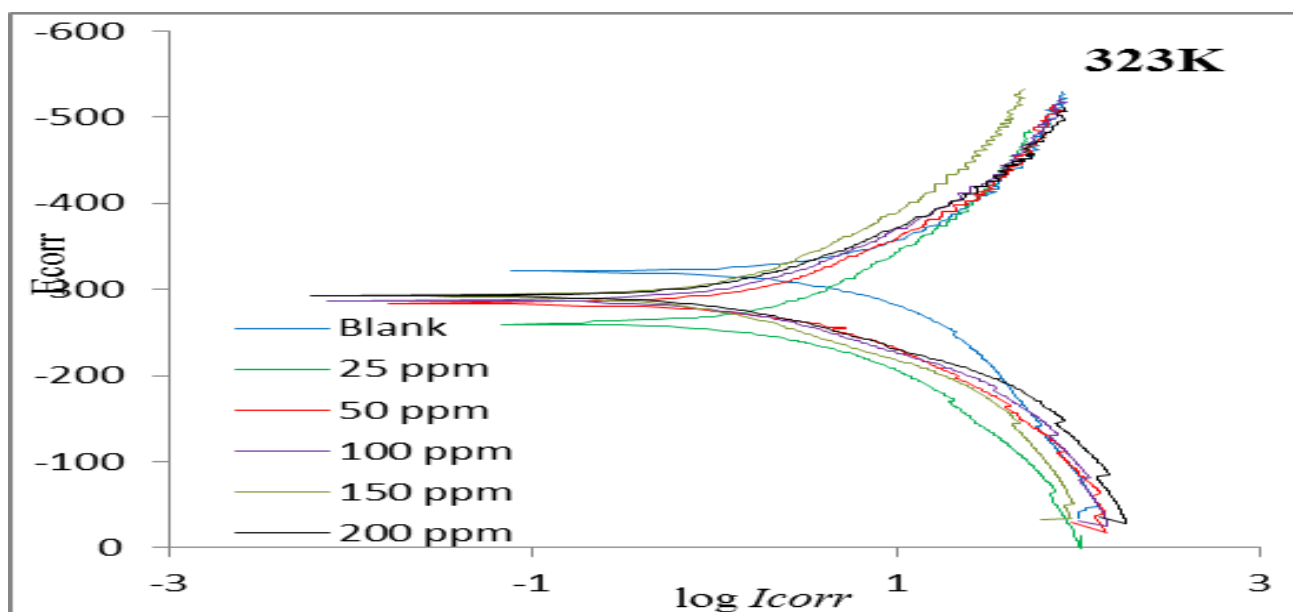
Rising the temperature at a stationary concentration of the inhibitor rises the i_{corr} and the E_{corr} turns to a slightly active direction in 1M sulfuric acid concentration . The values of Tafel slopes (β_a , β_c) changed with rising in temperature from (303-323)K decreasing in β_a and β_c may be attributed to changing in method of anodic and cathodic reaction so this outcome it's because inhibition of hydrogen reduction [17, 19].



"Figure 1: Polarization curves of the carbon steel in 1M H₂SO₄ solution and in the presence of different concentrations of methyl violet dye at the temperature 303K"



"Figure 2: Polarization curves of the carbon steel in 1M H₂SO₄ solution and in the presence of different concentrations of methyl violet dye at the temperature 313K"



"Figure 3: Polarization curves of the carbon steel in 1M H₂SO₄ solution and in the presence of different concentrations methyl violet dye at the temperature 323K"

Table 1: polarization parameters for the corrosion of carbon steel by different concentrations of methyl violet dye in 1M H₂SO₄ at the temperature range (303-323) K"

Temp. (K)	Inhibitor Conc. (ppm)	E _{corr} - M V)(I _{corr} A/cm ² ($\frac{a\beta}{mV/dec}$ ($\frac{c-\beta}{mV/dec}$	% η	θ
303	0	439.8	1020	52.3	89.1	0	0
313		382.2	1810	73.9	73.0	0	0
323		319.8	3880	91.3	90.1	0	0
303	25	384.8	437.15	40.3	84.0	57.14	0.5714
313		350.8	689.18	47.4	74.8	61.92	0.6192
323		260.7	1420	58.3	88.5	63.40	0.6340
303	50	320.6	362.01	37.6	76.6	64.50	0.6450
313		361.7	581.99	43.1	72.0	67.84	0.6784
323		284.4	1070	47.1	68.4	72.42	0.7242
303	100	327.2	328.30	45.6	90.0	67.81	0.6781
313		359.3	546.94	48.8	65.6	69.78	0.6978
323		287.7	871.56	54.8	66.9	77.53	0.7753
303	150	329.3	260.23	43.3	86.8	74.48	0.7448
313		351.3	371.49	45.0	91.4	79.47	0.7947
323		292.4	676.72	64.7	66.1	82.55	0.8255
303	200	356.1	193.25	48.4	87.8	81.05	0.8105
313		338.0	309.50	36.9	51.8	82.90	0.8290
323		291.9	647.89	44.4	55.6	83.30	0.8330

Kinetics of Corrosion

The influence of temperature on the corrosion rate at multiple temperatures (303-323) K

and the kinetic variables of the corrosion process were elaborate by similar Arrhenus equation (2) [20].

$$\log i_{corr} = \log A - \frac{E_a}{2.303 RT} \dots\dots\dots (2)$$

Where i_{corr} : corrosion current density, A; Arrhenius constant, E_a : activation energy, R: the gas constant, T: the temperature of the solutions .

Figure (4) show the diagram between Log i_{corr} versus $1/T$ for carbon steel corrosion in 1M of H₂SO₄ in the absence and the existence of diversified concentrations of methyl violet dye where the activation energy was

extracted from the slope of the drawn relationship and Log A was extracted from intercepts the drawn relationship. In order that take out additional information about the corrosion process the energies of activation, enthalpy ΔH^* , entropy of activation ΔS^* and Gibbs free energy ΔG^* were calculated via the equations below (3, 4) [21].

$$i_{corr} = \frac{RT}{Nh} e^{\left(\frac{\Delta S^*}{R}\right)} e^{\left(-\frac{\Delta H^*}{RT}\right)} \dots\dots\dots (3)$$

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

Where N: Avogadro's number, h: is Plank's constant Figure (5) display the linear relationship between the Log i_{corr} / T versus $1/T$, slopes $(-\Delta H^*/2.303R)$ and intercepts $(\log R/Nh + \Delta S^*/2.303R)$. Table (2) shows values E_a , A, ΔH^* , ΔS^* , ΔG^* . Some studies have indicated that the presence of inhibitors leads to reduced activation energy and this explains the occurrence of physical adsorption [22, 23]. The positive values of activation enthalpy (ΔH^*) for dissolution reaction of carbon steel in the medium of 1M H₂SO₄ in the absence and the existence of

several concentrations of methyl violet dye indicate that the reaction is endothermic operation and slow [24, 25].

The negative values of entropy activation signalize the formulation of the activated complex and the presence of an inhibitor increases the entropy values and is explained by the movement of reactants on the surface that turn into active adsorbent complexes on the surface, The positive values of Gibbs free energy signal the formation of the spontaneously activated complex according to the experimental conditions [26, 27].

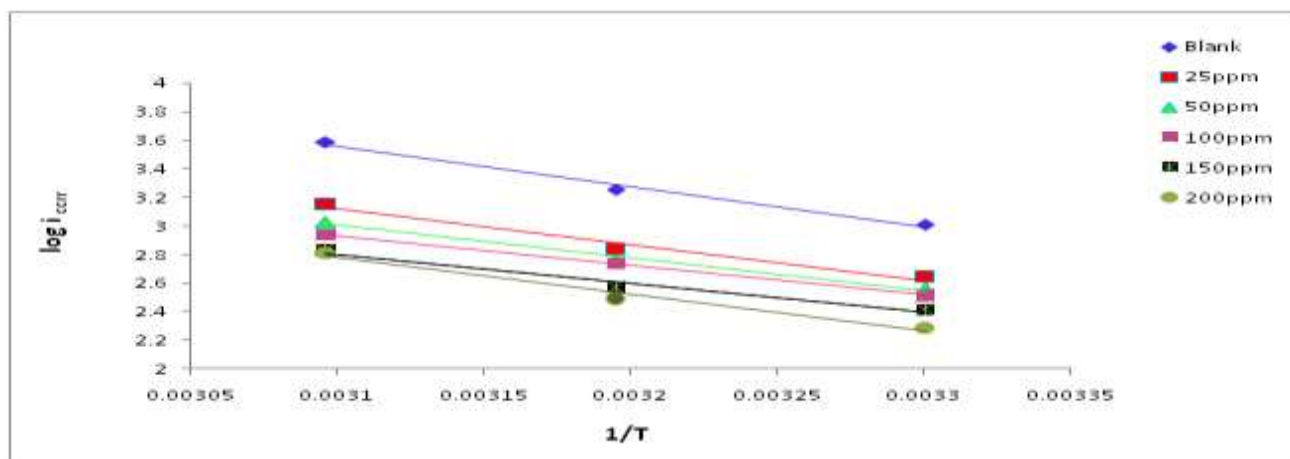
A linear relationship was found among experimental values for Log A and the correspondent values for E_a for carbon steel

corrosion at several concentrations of inhibitors used as shown in Figure (6) which can be expressed by equation (5) [28].

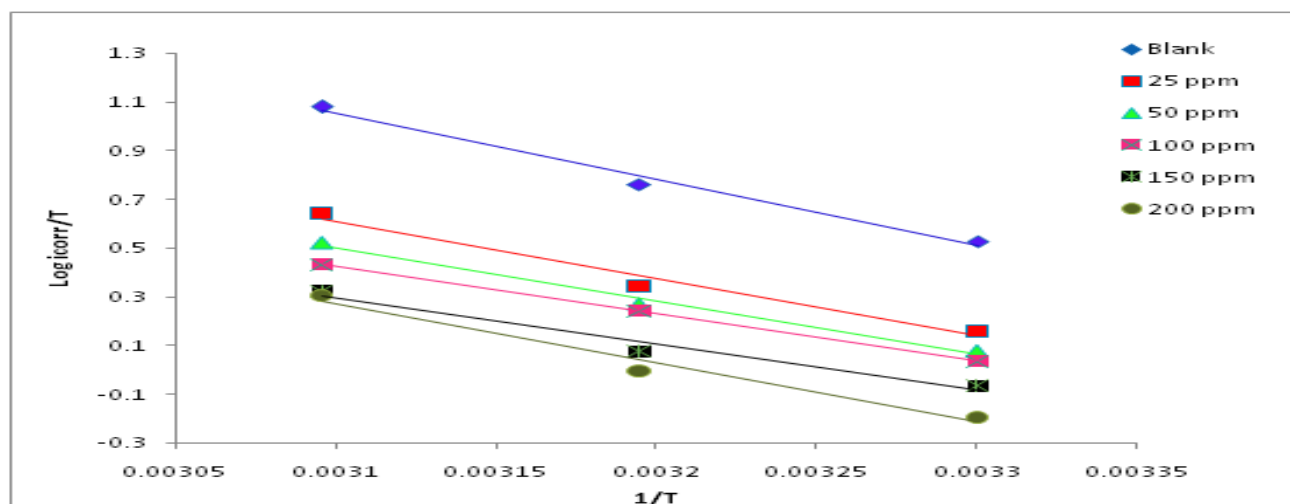
$$\text{Log A} = b + a E_a \dots\dots\dots (5)$$

Where the value of a and b are the constants. They slope and intercept the linear relationship, respectively. This relationship is called a "compensating effect", which explains the kinetics of catalytic reactions or reactions that cause soiling of the surface of a

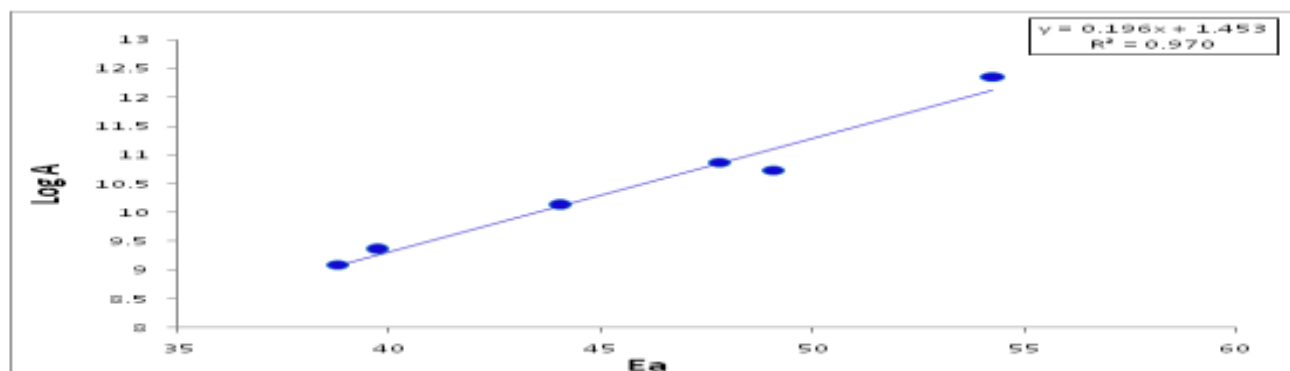
metal or alloy [29]. When the compensation effect is present, a noticeable difference in value E_a and log A may occur through a chain of locations on the surface of the metal to output slight difference in the reaction.



"Figure 4: Arrhenius plot of the carbon steel 1M H₂SO₄ at various Methyl Violet dye concentrations at the temperature range 303-323K"



"Figure 5 :Relationship between Log i_{corr}/T versus $1/T$ "



"Figure 6: E_a values are draw versus Log A for carbon steel .corrosion in (1M H₂SO₄) and different methyl violet dye concentrations at the temperature range 303-323K "

Table 2: values of E_a and A for corrosion of carbon steel in the presence and absence of several concentrations of methyl violet dye at a temperature of (303-323) K in 1M H_2SO_4

Comp.	Inhibitor Conc. (ppm)	E_a (kJ.mol ⁻¹)	A (Molecule.Cm ² ..S ⁻¹)
Methyl Violet dye	0	54.2649	2.218×10^{12}
	25	47.8084	7.244×10^{10}
	50	44.0250	1.367×10^{10}
	100	39.7360	2.323×10^9
	150	38.7691	1.198×10^9
	200	49.0932	5.333×10^{10}

Table 3: ΔH^* , ΔS^* , ΔG^* values for the corrosion of carbon steel in the presence and absence several of methyl violet dye concentration at temperature rang (303-323)K

Comp.	Inhibitor Conc./ (ppm)	ΔH^* (kJ.mol ⁻¹)	ΔS^* (kJ.mol ⁻¹ .K ⁻¹)	ΔG^* (kJ.mol ⁻¹)		
				303	313	323
Methyl Violet dye	0	51.6647	-0.01728	56.90054	57.07334	57.24614
	25	45.2064	-0.04573	59.06259	59.51989	59.97719
	50	41.4248	-0.05960	59.4836	60.0798	60.6756
	100	37.1339	-0.07433	59.65589	60.39919	61.14249
	150	36.1689	-0.07983	60.35739	61.15569	61.95399
	200	46.4930	-0.04828	61.12184	61.60464	62.08744

Thermodynamic of Corrosion Process

The Gibbs free energy for corrosion of carbon steel in 1M H_2SO_4 medium at several

temperatures (303-323)K. was calculated using the equation(6) [30].

$$\Delta G = -nFE_{\text{corr}} \dots\dots\dots (6)$$

N: The number of electrons flowing from the anodic, F: Faradays constant , E_{corr} : potential cell. The values of enthalpy (ΔH) for each concentration can be calculated by the values

of Gibbs free energy (ΔG) at different temperatures through the Helmholtz equation (7) [31].

$$\Delta G/T = \Delta H/T + \text{cons} \dots\dots\dots (7)$$

by the slope of the linear relationship between $\Delta G/T$ and $1/T$ as shown in Figure (7) .While ΔS can be calculated via the values

of .enthalpy ΔH and the values of the Gibbs free energy ΔG according to the following equation (8) [32].

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (8)$$

The thermodynamic amounts ΔG , ΔH and ΔS for carbon steel in.1M H_2SO_4 at three temperatures in extent.(303- 323)K are presented in Table(4) .the consequence display the negative values of ΔG that mean, the reaction is spontaneity and found ΔG raise with temperature,. Negative values of (ΔH) mean the reaction in exothermic nature,

the exothermic process involves either physisorption or chemisorption or of both the processes. The negative value of (ΔS) shows decreased the randomness. At the metal//solution interface. This lowering due to fewer water molecules adsorbed on to the metal surface [33, 34].

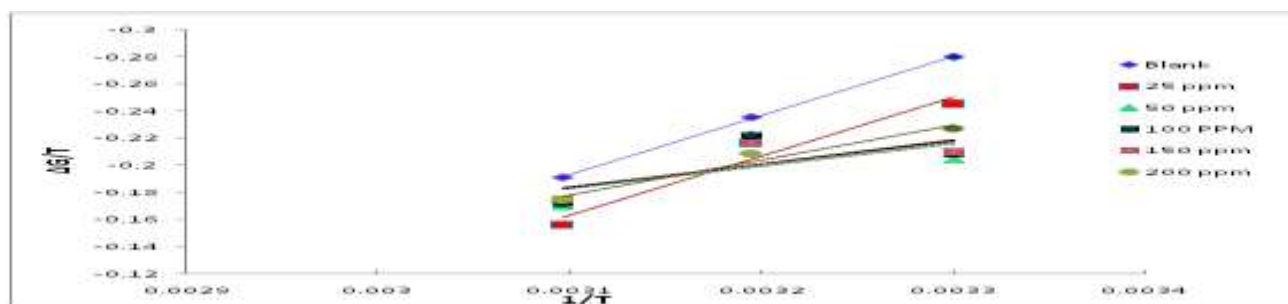
Figure.7: Relationship. Between $\Delta G/T$ versus $1/T$ for inhibition methyl violet dye in 1M H_2SO_4 at the temperature range 303-323K

Table 4: shows the thermodynamic quantities ΔG , ΔH and ΔS for the carbon steel in the presence and absence different methyl violet dye concentration at temperature rang (303-323)K

Temp. (K)	Inhibitor Conc.(ppm)	ΔG (kJ.mol ⁻¹)	ΔS (kJ.mol ⁻¹)	ΔH (kJ.mol ⁻¹)
303	0	84.8814-	-1.15748	- 435.6
313		-73.7646	-1.15602	
323		-61.7214	-1.15751	
303	25	-74.2664	-1.19162	- 435.33
313		-67.7044	-1.17452	
323		-50.3151	-1.19199	
303	50	-61.8758	-0.33677	-163.92
313		-69.8081	-0.30067	
323		-54.8892	-0.33755	
303	100	-63.1496	-0.37016	-175.31
313		-69.3449	-0.33854	
323		-55.5261	-0.37084	
303	150	-63.5549	-0.34750	-168.85
313		-67.8009	-0.33562	
323		-56.4332	-0.34803	
303	200	-68.7273	-0.61657	-255.55
313		-65.234	-0.60803	
323		-56.3367	-0.61675	

Thermodynamic of Inhibition Process, (Adsorption)

The adsorption demeanor of methyl violet dye can be explained by chemical or physical adsorption and the determination of the adsorption style on the surface of carbon steel

at several temperatures (303-323)K A linear rapport was acquired between C_{inh} / Θ and C_{inh} signalize the adsorption operation of Inhibitor by comply the (Langmuir) isotherm equation (9) [35].

$$\frac{C_{inh}}{\Theta} = \frac{1}{K_{ads}} + C_{inh} \dots\dots\dots (9)$$

Where C_{inh} : concentration of inhibitor. Θ : surface coverage, K_{ads} : adsorption constant. "

Figure (8) shows the linear relationship between C_{inh}/Θ versus C_{inh} whose intercepts are equal to $1 / K_{ads}$. The Gibbs free energy

values ΔG_{ads} . of the adsorption operation were extracted by compensating the adsorption constant value in the equation (10) [36].

$$\Delta G_{ads} = - RT \ln (55.5 K_{ads}) \dots\dots\dots (10)$$

Where T: temperature, R.: is the generic gas constant. The numerical value of 55.5 illustrates the molar concentration of water in acid solution. Figure (9) shows the rapport between values $\log K_{ads}$ and $1/ T$ for the

purpose of obtaining adsorption enthalpy from its slope depending on to the Van't Hoff equation (11) [37].

$$\log K_{ads} = \left(- \frac{\Delta H_{ads}}{2.303 R T} \right) + Con. \dots\dots\dots (11)$$

Then from the values of ΔG_{ads} and ΔH_{ads} ,

the ΔS_{ads} can be extracted by the equation (12).

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \dots\dots\dots (12)$$

Table (5) shows illustrates the thermodynamic of methyl violet dye on the carbon steel surface. The negative values of (ΔG_{ads}) for absorption reveal that the absorption of inhibitor molecules on the carbon steel surface is involuntary [38]. The positive value of the adsorption enthalpy (ΔH_{ads}) indicates that the adsorption of the

inhibitor molecules on the surface of the carbon steel alloy is an endothermic process. This means that the adsorption is chemically [39, 40]. The positive values of entropy adsorption (ΔS_{ads}) signalize the irregularity of the adsorbed layers on the superficies of the metal [29].

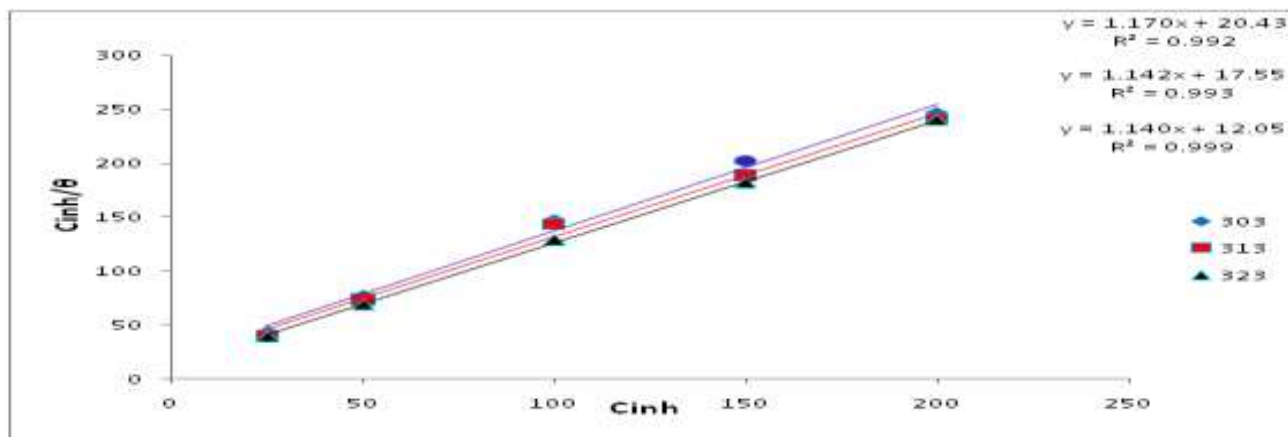
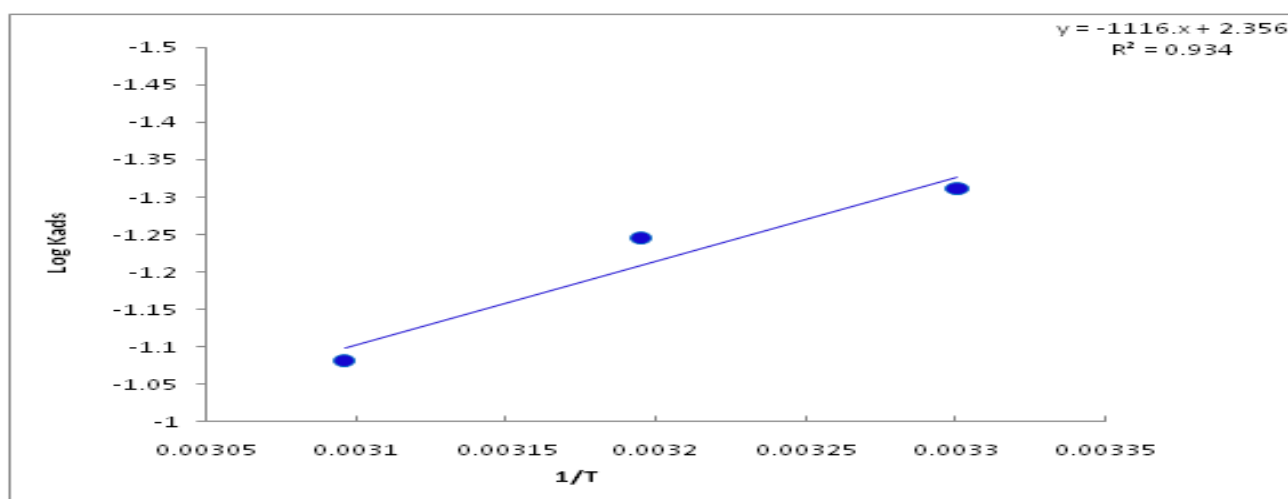


Figure8: Langmuir relationship methyl violet dye "adsorption in.1M H₂SO₄ at different temperature in the ambit (303-323) K "



"Figure 9: log K_{ads} with $1/T$ for carbon. Steel 1M H₂SO₄ in the presence of methyl violet dye"

"Table 5: The thermodynamic amounts of adsorption of methyl violet dye on carbon steel in 1M H₂SO₄ at temperature range (303-323)"

Compound	Medium Conc.(M)	Temp. (K)	K_{ads} (M ⁻¹)	$G_{ads}\Delta$ (kJ.mol ⁻¹)	ΔS_{ads} (kJ.mol ⁻¹ .K ⁻¹)	ΔH_{ads} (kJ.mol ⁻¹)
Methyl Violet dye	1M	303	0.0489	-2.5171	0.0788	21.3701
		313	0.0569	-2.9947	0.0778	
		323	0.0829	-4.1006	0.0788	

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