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Effect of Experimental Conditions on the Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium

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Abstract

The inhibition of carbon steel corrosion in an acidic hydrochloric acid (HCl) medium was studied using basic violet 1 dye as an effective inhibitor. The study aimed to evaluate the prevention of corrosion of mild steel in an acidic medium (hydrochloric acid) using an effective organic corrosion inhibitor, the dye basic violet 1. The study focused on evaluating the effect of different dye concentrations and temperatures on inhibition efficiency. Employing advanced electrochemical techniques such as polarized electrochemical current measurement, the analysis of the experimental results revealed significant effects as inhibitor concentration and temperature increased. The highest inhibition rates were recorded at the highest concentration and temperature studied. This is attributed to the adsorption of Basic Violet 1 molecules onto the steel surface, forming a protective layer that reduces anodic and cathodic reaction rates, indicating that the inhibitor acts in a mixed and effective manner. Furthermore, the electrochemical results showed that the protective layer is more stable at higher concentrations and that the inhibition mechanism involves both chemical and physical adsorption. This study concludes that Basic Violet 1 is an effective inhibitor of corrosion of mild steel in acidic environments. This study elucidates the relationship between dye concentration, temperature, and inhibition efficiency, providing a scientific basis for potential industrial applications in protecting steel from corrosion in harsh acidic environments. These findings represent a starting point for the development of novel and effective organic inhibitors.

Keywords: Corrosion inhibition, Adsorption mechanism, Organic inhibitors, Corrosion, Mild steel, Acidic medium.

1. Introduction

Corrosion of mild steel under acidic conditions is a major problem in many industrial processes, including acid pickling, cleaning, descaling, and oil and gas production. Because hydrochloric acid, commonly used to remove oxide layers, is highly effective, it increases the rate of corrosion of steel surfaces, leading to material deterioration, financial losses, and safety concerns [(1)]. To address this

issue, corrosion inhibitors are considered among the most efficient and economical methods for preventing corrosion of steel in acidic environments. Organic inhibitors are especially attractive because they contain heteroatoms such as nitrogen, sulfur, and oxygen, as well as aromatic rings, which enhance their ability to bond to metal surfaces [2,3]. The adsorption of these organic compounds creates a protective layer that mitigates both anodic metal dissolution and cathodic hydrogen evolution reactions [4,5]

Organic dyes have recently gained popularity as corrosion inhibitors, partly due to their complex chemical structures, availability, and high adsorption capacity [6,7]. Basic Violet 1 (Figure 1) has attracted considerable attention and made a substantial contribution to the prevention of carbon steel corrosion due to its aromatic structure and the presence of many nitrogen atoms. The alloy's characteristics enable more effective communication with the metallic surface through both physical and chemical adsorption. [8,9]

The aim of this research was to assess the effectiveness of a basic violet dye in preventing corrosion of carbon steel under acidic conditions via electrochemical processes. The research examined how inhibitor concentration and temperature influenced corrosion behavior. Polarization measurements were employed to evaluate current density and the effectiveness of the inhibitor. Additionally, thermodynamic and kinetic parameters were analyzed to deepen understanding of the inhibition mechanism [1]. This knowledge is essential for enhancing material durability and boosting the performance of industries working in acidic settings.

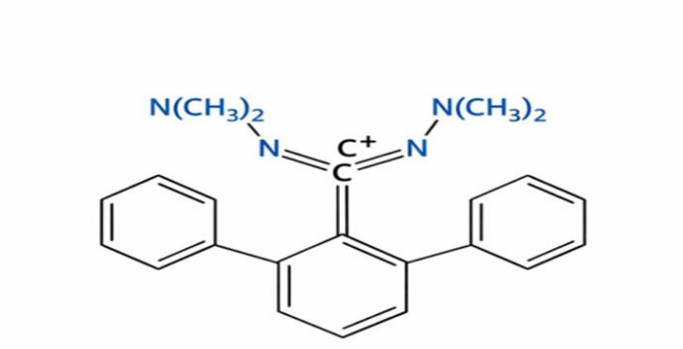

Figure 1. Chemical structure of Basic Violet 1, a triphenylmethane dye

2. EXPERIMENTAL PART

2.1 *Sample Preparation*

The specimens were made by cutting a mild steel columns into cylindrical samples approximately 2.5 cm in width and 3mm in height the chemical composition comprises 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, and 0.224% Cu, with Fe serving as the test sample. Reflective workmanship was achieved through mechanical polishing and smoothing using fine polishing tools and sanding boards of various grits (80-3500). After utilizing Microcloth with polishing paste, the samples were cleaned with 100% ethanol and dried till suitable for use.

2.2 Acid Solution Preparation

To make a 1 M hydrochloric acid (HCl) solution, cautiously dilute the concentrated solution of HCl (37%, density = 1.18 g/mL, ~12 M) with distilled water. To prepare 1 L of 1 M HCl, 83.3

mL of concentrated HCl was gradually added to about 900 mL of distilled water in a 1 L volumetric flask while stirring continuously. The solution was then further diluted with distilled water until it reached its final volume of 1 L.

2.3 Inhibitor Solution Preparation

Multiple concentrations of the Basic Violet 1 dye inhibitor were prepared in an acidic medium by accurately weighing the required amount of the inhibitor and dissolving it directly in 1 M hydrochloric acid.

2.4 Electrochemical Measurements

Electrochemical experiments were performed with a typical three-electrode cell coupled to a potentiostat/galvanostat. The working electrode was constructed of carbon steel, the reference electrode was a saturated calomel electrode (SCE), and the auxiliary electrode was a platinum plate. The functioning electrode was submerged in the test solution for 30 minutes before each measurement, thereby allowing the entire system to stabilize at its open-circuit voltage. The studies were carried out in 1.0 M hydrochloric acid solution, with and without varying inhibitor doses, at varied temperatures. Potentiodynamic polarization experiments were performed by scanning the potential from -250 mV to +250 mV relative to the open-circuit potential (OCP) at a scan rate of 1 mV s^{-1}. The corrosion current density (I_corr) and corrosion potential (E_corr) have been estimated by extrapolating segments of linear geometry from the anodic and cathodic Tafel slopes. The inhibitory effectiveness (η%) was estimated using the following mathematical equation:

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

where Icorr and Iinh are the corrosion current densities in the absence and presence of the inhibitor, respectively.

3. RESULTS AND DISCUSSION:

3.1 *Effect of Inhibitor Concentration*

It was found that the electrochemical values depend primarily on the inhibitor concentration when preventing carbon steel corrosion in an acidic environment. Increasing the concentration of the organic inhibitor significantly decreased the corrosion current density, thereby enhancing the inhibition efficiency. Table 1 and Figure 2 show that the highest temperature and concentration achieved the inhibition efficiency of 93%. [10,11] This is consistent with previous studies showing that optimizing the concentration enhances adsorption of organic inhibitor molecules onto the mild steel surface, forming a robust protective layer that reduces both anodic and cathodic reactions. [12,13]

3.2 *Effect Of Temperature On Inhibition Efficiency*

Examines the relationship between temperature and inhibition efficiency at various concentrations. The study found an increase in inhibition efficiency with increasing temperature from 303K to

333K, as shown in Figure 2. This increase indicates that the inhibitor used is more effective at higher temperatures, which is consistent with recent studies on inhibitors' mild steel corrosion in acidic environments using various organic compounds [14-16]

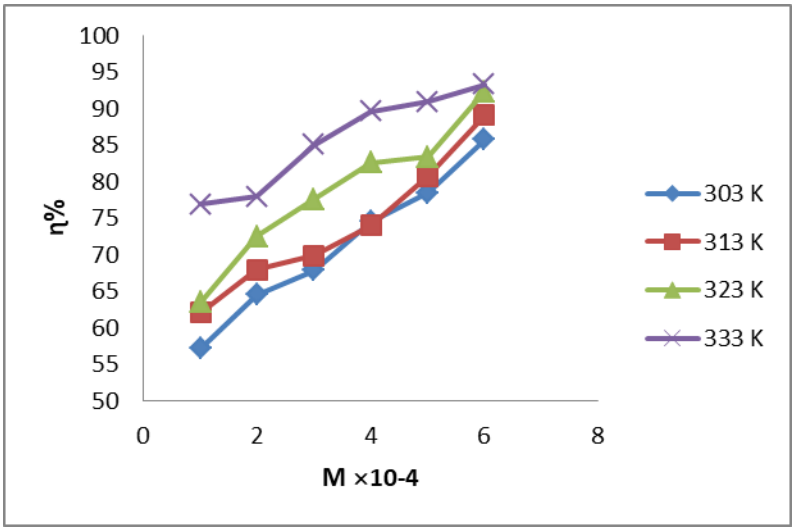

Figure 2. Efficiency of Inhibition in Relation to Concentration at Different Temperature Settings

Table 1 shows the numerical values of the dye's inhibition efficiency at different concentrations and temperatures, indicating that the peak efficiency, approximately 93%, was achieved at the highest concentration and temperature. This is accomplished by the adsorption of inhibitor molecules onto the surface of mild steel, generating a strong protective coating that inhibits the rates of anodic and cathodic reactions, a conclusion supported by recent research. [17,18] This behavior also demonstrates that the inhibitor exhibits mixed inhibition properties, affecting both anodic and cathodic reactions and maintaining its effectiveness within the studied temperature range [19,20]

Table (1): Corrosion characteristics and inhibitory effectiveness of Basic Violet 1 dye on mild steel in 1 M hydrochloric acid solution at numerous concentrations and temperatures.

Temp. K	Concentration M ×10^{-4}	-E_{corr} (M V)	I_{corr} (A/cm^2)	% η	θ	CR (mm/year)
303	Blank (no Inhibitor)	439.8	1020	0	0	2.37 × 10^{-5}
313		382.2	1815	0	0	4.21 ×10^{-5}
323		319.8	3882	0	0	9.00 ×10^{-5}
333		386.0	7120	0	0	1.65 ×10^{-4}
303	0.614	384.8	437.15	57.14	0.5714	1.01×10^{-5}
313		350.8	689.18	62.02	0.6202	1.60×10^{-5}

323		260.7	1420	63.42	0.6342	3.30×10^{-5}
333		378.9	1650	76.82	0.7682	3.83×10^{-5}
303	1.23	320.6	362.01	64.50	0.6450	8.40×10^{-6}
313		361.7	581.99	67.93	0.6793	1.35×10^{-5}
323		284.4	1070	72.43	0.7243	2.48×10^{-5}
333		334.2	1570	77.94	0.7794	3.64×10^{-5}
303	2.46	327.2	328.30	67.81	0.6781	7.62×10^{-5}
313		359.3	546.94	69.86	0.6986	$1..27 \times 10^{-5}$
323		287.7	871.56	77.54	0.7754	2.02×10^{-5}
333		284.4	1070	84.97	0.8497	2.48×10^{-5}
303	3.69	329.3	260.23	74.48	0.7448	6.04×10^{-5}
313		366.5	472.16	73.98	0.7398	1.10×10^{-5}
323		292.4	676.72	82.56	0.8256	1.57×10^{-5}
333		350.8	745.18	89.53	0.8953	1.73×10^{-5}
303	4.92	356.1	220.25	78.40	0.7840	5.11×10^{-6}
313		338.0	350.50	80.68	0.8068	8.13×10^{-6}
323		291.9	647.89	83.31	0.8331	1.50×10^{-6}
333		328.2	650.20	90.86	0.9068	1.51×10^{-5}
303	6.14	293.1	145.46	85.73	0.8573	3.37×10^{-6}
313		296.0	199.1	89.00	0.8900	4.62×10^{-6}
323		350.7	300	92.29	0.9229	6.96×10^{-5}
333		336.8	481.64	93.23	0.9223	1.12×10^{-5}

3.3. *Kinetic Parameters*

3.3.1 Activation Energy and Arrhenius Analysis

The kinetic progression of mild steel corrosion in a 1.0 M HCl solution has been investigated systematically, both without and with different inhibitor concentrations, using polarization measurements at various temperatures [21-23]. The corrosion current density (Icorr) was calculated for each temperature, and ln(Icorr) was plotted against the inverse of the absolute temperature (1/T) in line with the Arrhenius equation

$$\mathrm{Ln}\, I_{corr} = \mathrm{Ln}\, A - \frac{E_a}{RT} \qquad (2)$$

The activation energy (Ea) and the Arrhenius factor (A) were calculated using the slope and cross-section of the straight line.

The kinetic values were arranged from the lowest to the highest inhibitor concentration. An increase in the inhibitor concentration resulted in a gradual decrease in activation energy (Ea), indicating the formation of a stable, adsorbed protective layer on the steel surface that effectively reduces the corrosion rate. Likewise, the Arrhenius coefficient (A) decreased with increasing inhibitor concentration, reflecting a reduced frequency of active electrochemical events on the steel surface [24-26]. These findings are consistent with the inhibition efficiencies derived from polarization measurements. The calculated kinetic values are summarized in Table 2, and the corresponding Arrhenius curves are shown in Figure 3, demonstrating a clear trend of decreasing activation energy and Arrhenius coefficient as inhibitor concentration increases.

Table (2): Activation energy (Ea) and the Arrhenius pre-exponential factor (A) for the corrosion procedure for mild steel when using different inhibitor concentrations.

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Concentration M $\times 10^{-4}$	E_a ($kJ.mol^{-1}$)	A (A/cm^{-2})
Blank (no Inhibitor)	55.2	**3.3×10^{12}**
0.614	42.0	**6.0×10^{9}**
1.23	39.6	**3.3×10^{9}**
2.46	33.8	**2.3×10^{8}**
3.69	33.5	**8.2×10^{7}**
4.92	32.6	**9.8×10^{7}**
6.14	29.7	**3.9×10^{7}**

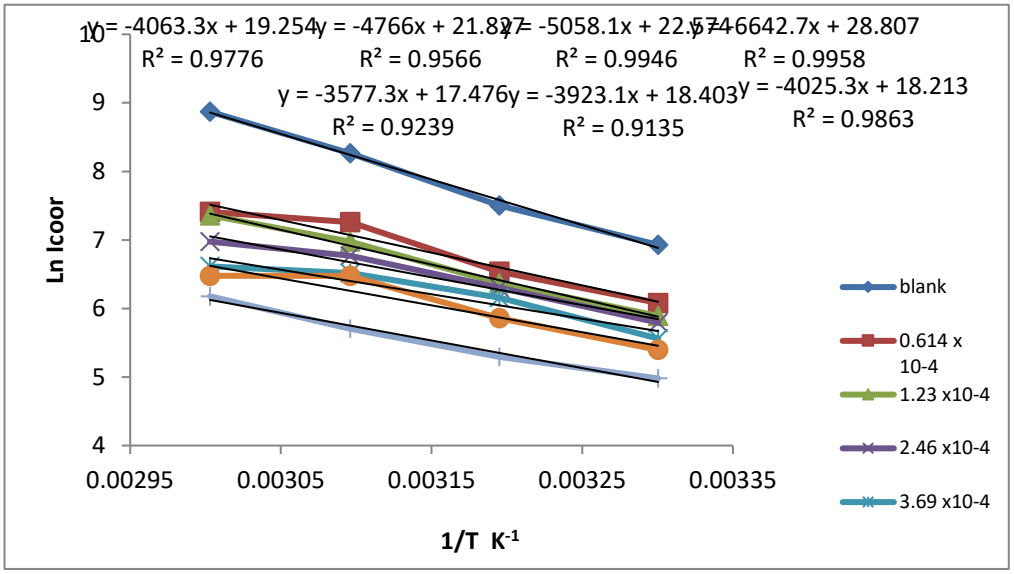

Figure 3. Arrhenius Diagrams (ln Icorr plotted against 1/T) for the Corrosion of Mild Steel at Varying Inhibitors.

3.3.2 Corrosion Rate

Table 1 shows that the corrosion rate of mild steel in an acidic environment decreases as the concentration of the organic inhibitor increases, with the highest concentration yielding the lowest corrosion rate. The diminution is related to the efficient adsorption of inhibitor molecules onto the steel surface, which forms a protective coating that hinders oxidation processes at the anode and hydrogen reduction reactions at the cathode, thereby reducing metal degradation. [27,28]

Changes in values were observed at low concentrations and across various temperatures, with the corrosion rate briefly increasing at specific intervals. This behavior is common in electrochemical Tests and is related to the overall heterogeneity of the surface or to the instability of the protective barrier at low concentrations [23,29]

The clear inverse relationship between corrosion rate and inhibition efficiency indicates that a lower corrosion rate corresponds to a higher inhibition efficiency, showcasing the inhibitor's effectiveness under all experimental conditions. These findings are consistent with prior research confirming the potential of organic inhibitors and pigments to form durable protective layers on mild steel under acidic conditions. [10,11,30]

3.4 Thermodynamic functions

The thermodynamic attributes of mild steel in an acidic Solution have been investigated at different levels of the Organic inhibitor and at different temperatures. The standard enthalpy ΔHo was estimated from the slope of the graph (ln lcorr/T) versus 1/T, using the modified Arrhenius equation derived from transition-state theory.

$$Ln\frac{I_{corr}}{T} = \frac{R}{Nh} + \frac{\Delta S*}{R} - \frac{\Delta H*}{RT} \qquad (3)$$

The standard entropy ΔSo was determined from the intercept by multiplying it by R, which reflects the change in randomness during the adsorption process. The retrieved quantities for ΔHo and ΔSo

show that the inhibitor adsorption onto the mild steel surface is an endothermic process Ho> 0) and increases the system's randomness (So>> 0). This is because the inhibitor molecules require energy to adhere to the surface, whereas some water molecules or ions are released, thereby increasing the system's overall randomness. The Gibbs compression energy ΔG^{o} was assessed for each concentration and temperature through the following calculations:

$$\Delta G^{*}=\Delta H^{*}-T\Delta S \qquad (4)$$

Most values indicate a semi-spontaneous process, with one negative value at a particular concentration, indicating a more stable and spontaneous adsorption state. The overall trends of these functions are illustrated in Figure 4, and the numerical data for each concentration and temperature are provided in Table 3.

The results reported here are consistent with previous investigations on corrosion inhibition that involved organic inhibitors and dyes in acidic conditions, which demonstrated that elevating the concentration of the inhibitor enhances the thermal stability of the protective covering and eliminates randomness on the metal surface [17,18,24,31]

Table 3. Thermodynamic metrics for Mild Steel in a 1M HCl medium at diverse concentrations of organic inhibitors and several temperatures (ΔH^{o}, ΔS^{o}, ΔG^{o})

Concentration M ×10-4	ΔH^{o} kJ.mol^{-1}	ΔS^{o} kJ.mol^{-1} .K^{-1}	ΔG^{o} kJ.mol^{-1}			
			303	313	323	**333**
Blank (no Inhibitor)	52.58	0.16	4.10	2.50	0.90	**-0.70**
0.614	36.98	0.10	6.68	5.68	4.68	**3.68**
1.23	39.41	0.11	6.08	4.98	3.88	**2.78**
2.46	31.14	0.08	6.90	6.10	5.30	**4.50**
3.69	27.10	0.06	8.92	8.32	7.72	**7.12**
4.92	29.97	0.07	8.76	8.06	7.36	**6.66**
6.14	30.82	0.07	9.61	8.91	8.21	**7.51**

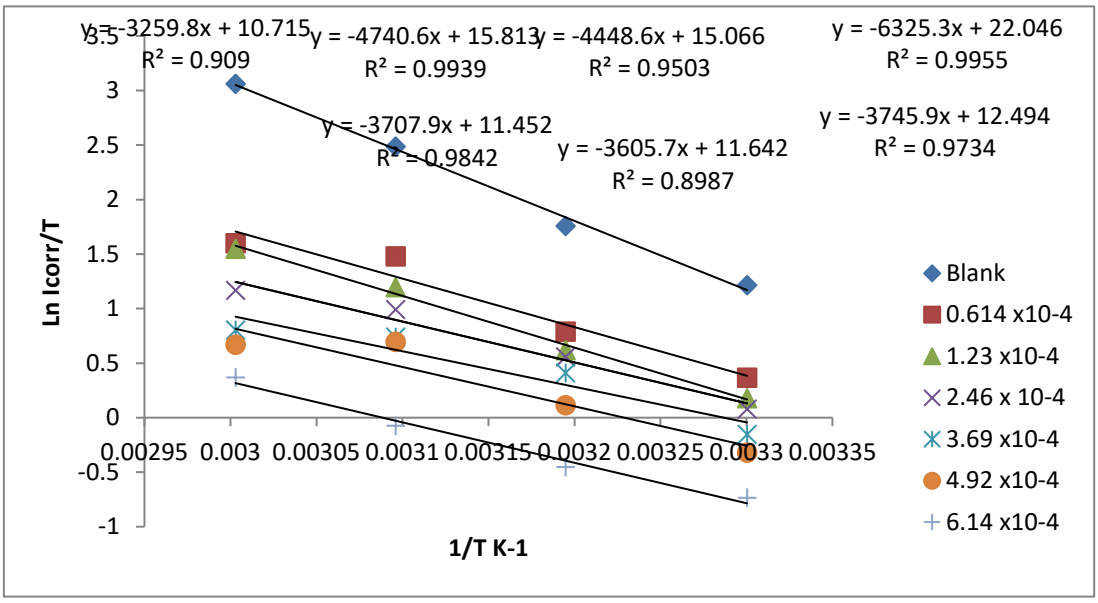

Figure 4 . Graphing ln($I_{(corr)}$/T) against 1/T to determine the thermodynamic properties (ΔH^{o} and ΔS^{o}) of Mild Steel with varying concentrations of organic inhibitor in 1M HCl.

3.4.1 Adsorption Isotherms and Thermodynamic Analysis

An investigation into the absorption behavior of the inhibitor on the Mild Steel surface in a 1 M HCl solution was carried out using adsorption isotherms. The Langmuir adsorption isotherm model provided an excellent fit with the experimental data, as shown in Figure 5 and Table 4. The linear graph of C/θ versus inhibitor concentration at various temperatures demonstrates the stability of the absorption coefficient Kads (Figure 5), with a complete correlation coefficient R=1, confirming that the absorption adheres closely to the Langmuir model, resulting in a uniform monolayer on the surface (32,33). The linear expression of the Langmuir model is:

$$\frac{C_{inh}}{\theta} = \frac{1}{\text{Kads}} + C_{inh} \qquad (5)$$

where C is the concentration of the inhibitor, θ is the surface coverage degree, and K is the constant for adsorption equilibrium. The value of K was extracted from the chart's y-intercept.

Thereafter, the calculation of the free energy of adsorption (ΔG°ads) was performed using the equation:

$$\Delta G_{ads} = -RT \text{ Ln } (55.5 \text{ K}_{ads}) \qquad (6)$$

where R is the gas constant, T is the temperature in Kelvin, and 55.5 reflects the concentration of water in mol/L for the standard state conversion. Negative values

of ΔGo ads indicate that the adsorption is spontaneous and stable [32,34]. To analyze the other thermal functions, we utilized a plot of Ln Kads against 1/T according to the Van't Hoff equation [35]. See Figure 6

$$Ln\ K_{ads.} = \left(-\frac{\Delta H\ ads.}{R\ T}\right) + Con \qquad (7)$$

The slope indicates that positive ΔHo ads values imply that adsorption is an endothermic process, suggesting that energy is required to release water molecules and surface-bound ions from the adsorption sites (36,37). The standard entropy change (ΔSo ads) was assessed for each temperature based on the relationship:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (8)$$

The favorable results suggested that randomness at the metal/solution interface developed when water molecules were released, and inhibitor molecules circulated across the surface. These findings suggest that adsorption occurs through a range of physical and chemical mechanisms, resulting in a stable monolayer that reduces the corrosion rate. Recent research has validated these findings [38,39]

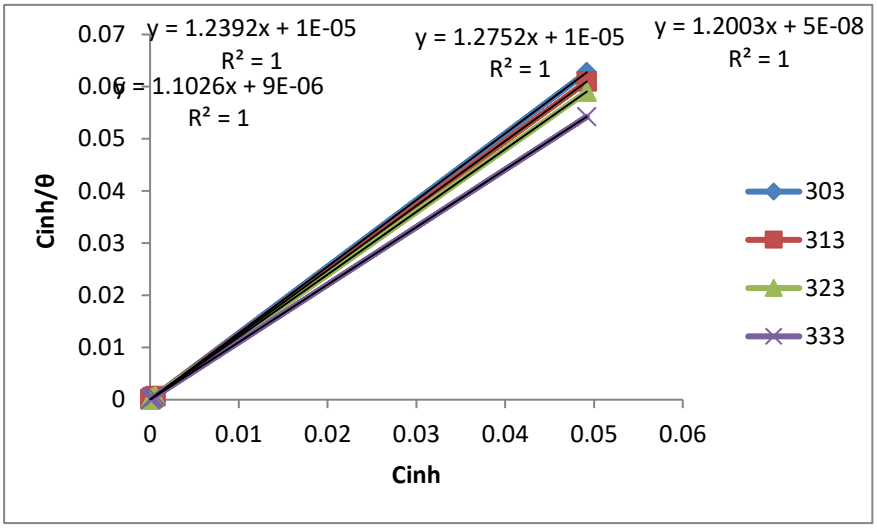

Figure 5. In the linear graph of the Langmuir model: plotted (C inh / θ) against inhibitor concentration at multiple temperatures.

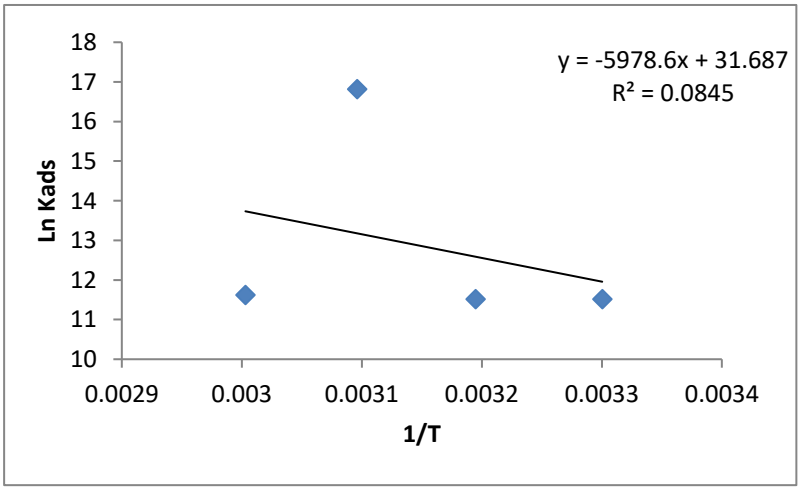

Figure 6 Thermal analysis of absorption: plotting ln(Kads) linearly versus 1/T to ascertain ΔH°ads for the corrosion inhibitor in a 1 M HCl solution

Table 4.The computed values of ΔG°ads, ΔH°ads, and ΔS°ads for the corrosion inhibitor at different temperatures in a 1 M HCl solution.

Medium Conc./M	Temp. (K)	k ads (M^{-1})	Δ Gads (kJ.mol^{-1})	ΔS ads (kJ.mol^{-1}.K^{-1})	ΔH ads (kJ.mol^{-1})
1M	303	1x10^5	-39.1	0.29	**49.70**
	313	1x10^5	-39.1	0.28	
	323	2x10^7	-58.7	0.33	
	333	1.11x10^5	-43.2	0.27	

4. Comparison with previous studies

The research demonstrated that the basic violet 1 inhibitor on the surface of stainless mild steel in 1M HCl exhibited increased activation and surface coverage with increasing concentration and temperature, reaching a peak effectiveness of approximately 93% at higher concentrations and temperatures. Estimates of ΔGo ads indicated selective, stable interception, while positive values for ΔHo ads and ΔSo ads suggested a random disappearance of neutrophils at the metal/solution interface. Analysis of a specific function.

The corrosion reaction rate (Icorr) and the activation energy (Ea) calculation confirmed that the inhibitor selectively absorbs the energy required for the corrosion reaction, thereby increasing its effectiveness.It is important to note that the comparison with previous research was conducted under similar conditions (1 M HCl and similar temperatures). Recent studies. [40-42] . have indicated similar behavior for organic inhibitors, with kinetic and thermodynamic functions showing a strong correlation with the Langmuir model (R2=1). This confirms the inhibitor's efficacy in forming a stable protective layer and reducing the corrosion rate under various experimental conditions.

5.CONCLUSION

- The inhibitor Basic Violet 1 has shown considerable efficacy in reducing the corrosion of mild steel in a 1M HCl solution, achieving a maximum efficiency of about 93% at the highest concentration and temperature, with a stable adsorbent layer forming on the surface .

- The thermodynamic values (ΔGoads , ΔHoads, ΔSo ads) indicated that adsorption process is spontaneous and endothermic , resulting in increased randomness on the metal surface, thereby supporting the interpreating of inhibitors molecular behaviour.
- The kinetic functions and activation energy (Ea) demonstrated that the inhibitor lowers the energy needed for the corrosion reaction, which in turn boosts its effectiveness and confirms its protective function for the metal .
- When compared to previous studies, the current results were found to be consistent with the behavior of similar organic inhibitors, thereby enhancing the credibility of the findings and affirming the inhibitor's effectiveness under a broad spectrum of experimental conditions.
- The results suggest that Basic Violet 1 can be utilized as a viable and effective approach to reduce corrosion in acidic environments, with the possibility of applying these results to future investigations involving other organic inhibitors or different conditions.

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