

Corrosion Inhibition of Carbon Steel in Acidic Solution by Alizarin Yellow GG (AYGG)

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Abstract

Alizarin yellow GG (AYGG) is a natural dye used as a corrosion inhibitor. The inhibitive action of this compound against corrosion of carbon steel in hydrochloric acid solution (1M concentration), has been tested using the weight loss measurements and electrochemical measurements techniques. The results indicates this compound is a good inhibitor for carbon steel in hydrochloric acid solution, and the inhibition efficiency increased as the concentration of this compound increased. Also the results revealed as the temperature increased, efficiency and corrosion activation energies are increased. On the basis of the experimentally determined activation energy values, the addition of this compound can be considered chemisorption adsorbed.

Keywords: Metals; Electrochemical techniques; Chemisorptions; Corrosion

Introduction

Due to increasing industrial applications of steel in acidic solution, study of corrosion phenomena of this metal in acidic solution is so important [1]. The main problem of using carbon steel is its dissolution in acidic solutions [2]. Hydrochloric acid is often used as a pickling acid for iron and its alloys in order to remove corroded metal or any scale formed on surface of the metal. After removal of undesirable rust or scale, the acid used, now is free for further attack on the metal surface. In order to prevent or retard metal dissolution and also reduce acid consumption, corrosion inhibitors are frequently used [3].

Corrosion can be controlled by suitable modification of the environment which in turn stifle, retard or completely stop the anodic or cathodic reactions or both. This is achieved by the use of proper inhibitors. Inhibitors which prevent corrosion are substances which when added to solution in small concentration can decrease or prevent the reaction of the metal with the solution [4].

These compounds can slow down the rate of corrosion processes by;

- Increasing the anodic or cathodic polarization behavior (Tafel slopes)
- Reducing the movement or diffusion of ions to the metallic surface
- Increasing the electrical resistance of the metallic surface

Anodic inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. Cathodic inhibitors either slow down the cathodic reaction, or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms:

1. As cathodic poisons,
2. As cathodic precipitates, and

3. As oxygen scavenger. Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a general rule, organic inhibitors affect the entire surface of a corroding

metal when present in sufficient concentration. Organic inhibitors usually designated as film-forming, which protects the metal by forming a hydrophobic film on the metal surface [5].

Organic inhibitors are applied extensively to protect metals from corrosion in many aggressive acidic solution (e.g. in the acid pickling and cleaning processes of metals). Most of these organic inhibitors are nitrogen, sulfur or oxygen containing compounds. The first stage in the action mechanism of these organic inhibitors in aggressive acid solution is their adsorption on the metal surface. The effectiveness of the functional atom in the adsorption processes varies according to the following sequence: S > N > O [6].

Most of commercially pickling inhibitors available are toxic compounds, for this reasons many investigators have tried to replace these compounds with new environmentally friendly inhibitors [7]. Due to this fact several different compounds have been investigated as natural corrosion inhibitors; such as, natural honey, berberine, caffeic acid, and etc [8-11].

Alizarin yellow GG (AYGG) $C_{13}H_8N_3NaO_6$ (an azo dye) [5-(3-nitrophenylazo)-2-hydroxybenzoic acid sodium salt] is a natural dye and it is considered to be an environmentally friendly compound, used in H_2SO_4 Solution [12].

In the present paper, by employing this compound (AYGG), the corrosion behavior of carbon steel in 1M HCl, has been studied, using the weight loss, polarization measurements and electrochemical impedance spectroscopy methods. The molecular structure of AYGG used in this study is shown in Figure 1.

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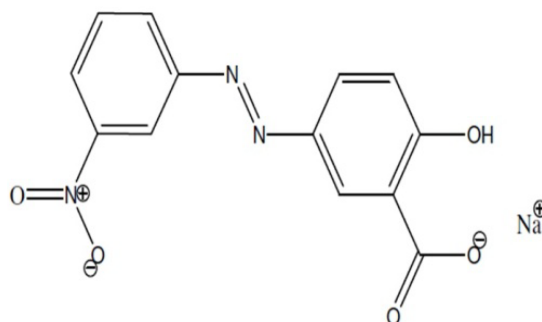


Figure 1: Molecular structure of Alizarin yellow GG (AYGG).

Medium (g/l AYGG)	Temperature								
	25°C			40°C			60°C		
	W (mg/cm ² h)	IE (%)	θ	W (mg/cm ² h)	IE (%)	θ	W (mg/cm ² h)	IE (%)	θ
0.0	0.37	-	-	1.152	-	-	8.23	-	-
0.003	0.324	12.8	0.128	1.011	12.2	0.122	5.554	32.5	0.325
0.02	0.228	38.8	0.388	0.696	39.6	0.396	5.178	37.1	0.371
0.09	0.222	40.3	0.403	0.255	77.9	0.779	0.260	96.8	0.968
0.25	0.020	94.5	0.945	0.060	94.8	0.948	0.221	97.3	0.973
0.3	0.014	96.1	0.961	0.038	96.7	0.967	0.22	97.3	0.973

Table 1: Corrosion parameters obtained from weight loss of carbon steel in 1 M HCl containing. Various concentrations of AYGG at different temperatures.

Experimental Procedures

Specimen preparation

In this study carbon steel with composition of 0.21% C, 0.38% Si, 0.09% P, 0.01% Al, 0.05% Mn, and 0.05% S) is used. Specimens were prepared from “Rose Corrosion Services Ltd”. Coupons were cut into 22 by 49 by 3 mm dimensions, used for weight loss measurements, and specimens with dimensions of 20 by 20 by 3 mm were used as working electrode for polarization and EIS measurements. The surface areas of these specimens were covered by polyester resin, leaving a surface area of 4 cm². The exposed area was mechanically abraded with 220, 400, and 800 and finally with 1200 grades of emery papers and polished by Al₂O₃ slurry, degreased with acetone and rinsed by distilled water before each electrochemical experiment.

Solutions preparation

1 M HCl solutions were prepared by dilution of 37% HCl (Merck brand) using distilled water. The concentration range of AYGG employed was varied from 0.003 to 0.3 g/l (3 to 300 ppm) and the electrolyte used was 800 ml for each experiment.

Weight loss measurements

Experiments were performed at temperature of 25, 40 and 60°C with different concentrations of AYGG. The immersion time for the weight loss was 6.5 h.

The inhibition efficiency (IE %) was calculated using the following equation:

$$IE\% = \frac{W_2 - W_1}{W_2} \times 100 \quad (1)$$

Where, W_1 and W_2 are the weight loss of the carbon steel in the presence and absence of inhibitor, respectively.

Polarization measurements

Electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell, containing 800 ml of electrolyte at the room temperature (25 ± 1°C). A saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrode, respectively. Polarization studies were conducted using computer controlled ZAHNER Elektrik model IM6eX potentiostat at a scan rate of 0.5 mV/s. THALES software was used for evaluating the experimental data. Before recording the polarization curves, the solution was de-aerated for 20 min and the working electrode was maintained at its corrosion potential for 25 minutes until a steady state was obtained.

The inhibition efficiency (IE %) was calculated using the following equation:

$$IE\% = \frac{I_2 - I_1}{I_2} \times 100 \quad (2)$$

Where, I_1 and I_2 are the corrosion current densities of carbon steel in the presence and absence of inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS)

EIS experiments were conducted using computer controlled ZAHNER Elektrik model IM6eX system with THALES software. Data from Zview software were used for calculation of polarization resistance (R_p) and double layer capacitance (C_{dl}).

All experiments were performed with a frequency ranging from 100 mHz to 10 kHz and peak-to-peak ac amplitude of 10 mV. The impedance diagrams were plotted in the Nyquist presentation form.

The inhibition efficiency (IE %) was calculated using the following equation:

$$IE\% = \frac{R_2 - R_1}{R_2} \times 100 \quad (3)$$

Where, R_1 and R_2 are polarization resistance of carbon steel in the absence and presence of inhibitor, respectively.

Results and Discussion

Weight loss measurements

The results obtained for evaluation of corrosion rate and inhibition efficiency for carbon steel in 1 M HCl solution at 25, 40 and 60°C in the absence and presence of AYGG are given in Table 1. The inhibition efficiency of AYGG as corrosion inhibitor for carbon steel, increased (up to 96.1%), with increasing concentration of this compound (tested at 25 ± 1°C). Also as one can notice, at temperature of 40 and 60°C, maximum inhibition efficiencies achieved for solution containing 0.3 g AYGG per liter of acid solution. The increase in corrosion rate is more pronounced with the rise of temperature for the uninhibited acid solution. As it is expected addition of the inhibitor used, leads to decrease of the corrosion rate. As it is mentioned above, the inhibition efficiency increases with both increase in AYGG concentration and temperature. This support the hypothesis, that the AYGG adsorption is more a chemisorption than a physisorption [13].

Polarization measurements

The result obtained from potentiodynamic polarization parameters of carbon steel immersed in different concentrations of AYGG, are given in Table 2 and the corresponding polarization curves are shown in Figure 2.

From results obtained in Table 2 the addition of AYGG decreases corrosion current density. Also, it can be clearly seen that the inhibition efficiency of AYGG increases with inhibitor corrosion concentration. This behavior is similar to weight loss results, which indicates that

Medium(g/l AYGG)	$-\beta_c$ (mV/dec)	E_{corr} (mV/SCE)	I_{corr} (mA/cm ²)	IE(%)
0.0	176	-462.3	0.3225	-
0.003	154	-476.1	0.1225	62
0.02	149	-367.1	0.0782	76
0.09	176	-454.5	0.0201	94
0.25	137	-342.7	0.0085	97
0.3	110	-471.4	0.0067	98

Table 2: Kinetic parameters of carbon steel in 1 M HCl at room temperature (25 ± 1°C) containing different concentrations of AYGG.

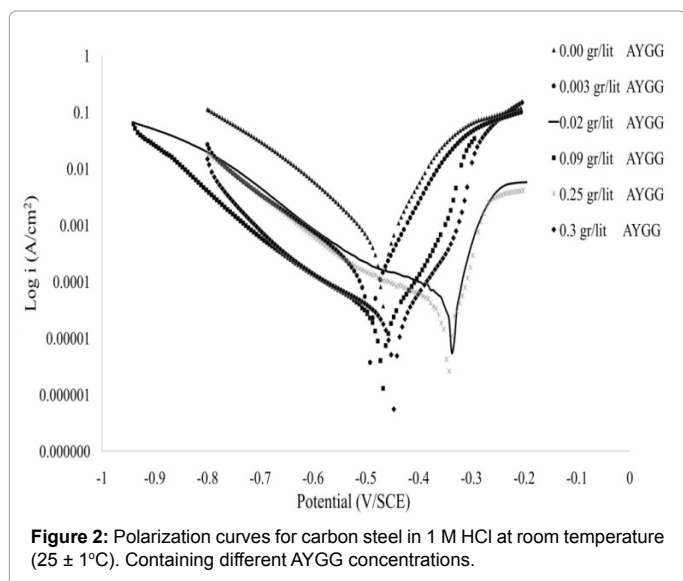


Figure 2: Polarization curves for carbon steel in 1 M HCl at room temperature (25 ± 1°C). Containing different AYGG concentrations.

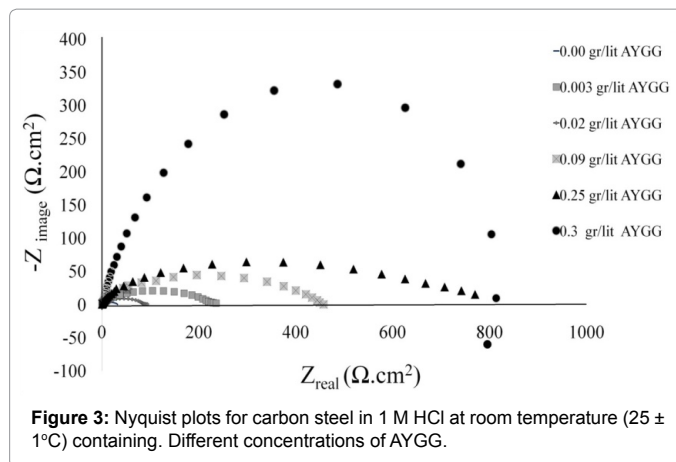


Figure 3: Nyquist plots for carbon steel in 1 M HCl at room temperature (25 ± 1°C) containing different concentrations of AYGG.

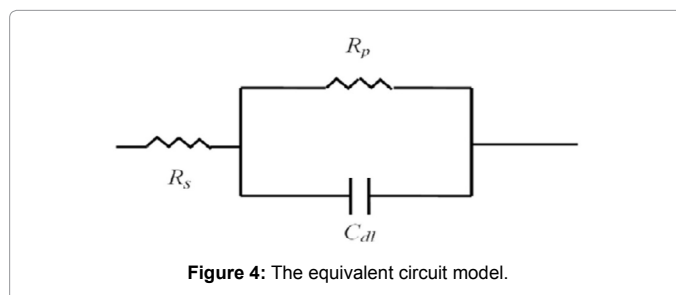


Figure 4: The equivalent circuit model.

AYGG acts as a good corrosion inhibitor for carbon steel in HCl solution.

According to polarization curves, the cathodic slopes Figure 2 decreased with increasing in the AYGG concentration, whereas, anodic slopes changes is in irregular manner. Moreover, in the presence of AYGG the values of corrosion potential E_{corr} vary from -462.3 to -342.7 (mV). Therefore, AYGG could be classified as a cathodic-type inhibitor [1]. The present results indicate a pervasiveness of the inhibitive effect, which implies that the Fe-dye complexes formed an insoluble surface layer which isolated the metal surface from the acidic solution. The integrity of this protective film has been shown to be quite sensitive to the AYGG concentration [14]. The curvature of the anodic branch may be attributed to the deposition of the corroded metal or impurities in the carbon steel (e.g., Fe_3C) which forms a non-passive surface film. In addition, inflection in the anodic branches is quite clear, which may be due to passivation of pitting [15].

Electrochemical impedance spectroscopy (EIS)

Figure 3 displays the Nyquist plots of specimens immersed for 30 minutes in HCl solution with different concentrations of AYGG at room temperature (25 ± 1°C). After analyzing the shape of the Nyquist plots, and considering the relevant spectra, the equivalent circuit shown in Figure 4 can be modeled. Where R_s represents solution resistance, R_p polarization resistance and C_{dl} double layer capacitance. As it is noticed the diameter of Nyquist plots (R_p) increases with increasing the AYGG concentration. From these results one may conclude that the AYGG acts as a corrosion inhibitor for carbon steel, in 1 M HCl solution. This suggested that, the formed inhibitive film was strengthened by addition of this corrosion inhibitor [16]. The obtained impedance diagrams have almost a semicircular appearance, indicating a charge transfer process which mainly controls the corrosion of carbon steel [17]. It is clear that the shapes of the impedance plots for inhibited electrodes are not

Medium(g/l AYGG)	R _p (Ωcm ²)	f _{max} (HZ)	C _{dl} (μF/cm ²)	IE(%)
0.0	28.88	65.55	84.12	-
0.003	88.69	34.71	56.4	67.4
0.02	205.1	13.07	59.4	85.9
0.09	412.4	89.57	43.11	92.9
0.25	655.1	57.72	42.12	95.59
0.3	762.6	20.70	101.07	96.2

Table 3: Impedance parameters of carbon steel in 1 M HCl at room temperature (25 ± 1°C) containing different concentrations of AYGG.

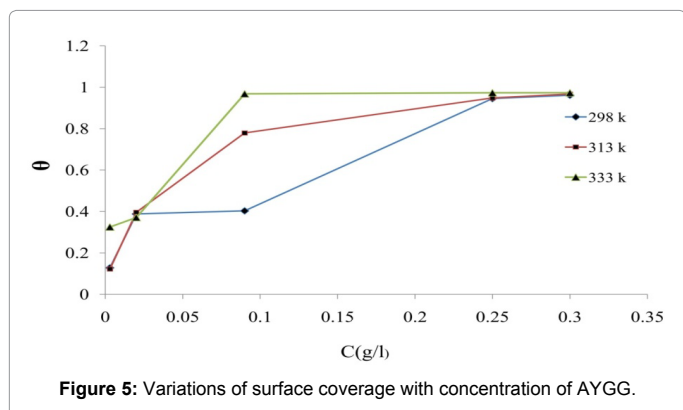


Figure 5: Variations of surface coverage with concentration of AYGG.

substantially different from those of uninhibited ones. The presence of the corrosion inhibitor increases the impedance but does not change other aspects of behaviors. These results support the findings of polarization measurements presented before, which shows that the corrosion inhibitor does not alter the mechanism of electrochemical reactions responsible for the corrosion. This phenomena is due to fact that no matter what the concentration of corrosion inhibitor is, addition of this compound primarily affect adsorption on the metal surface (chemisorption mechanism) [18].

As it is shown in Figure 3 for concentration of 0.3 g/l AYGG, the center of semicircular is below the real axis. This feature shows contribution from surface roughness, distribution of active sites, and adsorption of inhibitors and formation of porous layers as reported by others [19]. The EIS parameters are given in Table 3. Polarization resistance R_p increases from 28.88 to 762.6 Ω.m² with the increase of AYGG concentration. The increase in the polarization resistance leads to an increase of inhibition efficiency. The results indicate a good agreement between the values of corrosion efficiency obtained from the impedance technique and polarization measurements. It is concluded that the corrosion rate depends on the chemical nature of the electrolyte rather than the applied technique [20].

Adsorption isotherm behavior

The variations of surface coverage with concentration of AYGG at different temperatures are shown in Figure 5. As one can notice at high concentration of inhibitor, the inhibitory effect remained constant, suggesting complete saturation of the surface by the inhibitor molecules [20].

A correlation between surface coverage (θ) defined by (IE %) /100 and the concentration of inhibitor (C_{inh}) in electrolyte can be represented by the Langmuir adsorption isotherm,

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \quad (4)$$

Where, K is the adsorption constant. Figure 6 shows the dependence

of the ratio $\frac{C}{\theta}$ as function of the concentration of AYGG. The K values are given in Table 4. Since the efficiency of a given inhibitor is essentially function of the magnitude of its binding constant K, therefore, large K values mean better and stronger interaction, whereas small K values, mean the interaction between the inhibitor molecules and the metal is weaker. According to the K values, it is concluded that the interaction between the inhibitor molecules and the metal improved and the adsorption tendency of this compound on steel surface increased by increasing the temperature [21,22].

In order to calculate the energy of adsorption (ΔG_{ads}), following equation is used.

$$K = \frac{1}{55.5} e^{-\left(\frac{\Delta G_{ads}}{RT}\right)} \quad (5)$$

Where the value of 55.5 is the volume ratio of water content in solution in ml/l [18]. Figure 7 clearly shows the dependence of ΔG_{ads} on T, indicating a well correlation among thermodynamic parameters.

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (6)$$

The free energy of adsorption (ΔG_{ads}) values were calculated and given in Table 4. The negative values of ΔG_{ads} indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process.

The dependence of ΔG_{ads} on temperature can be explained by the following points [1];

- (a) ΔG_{ads} may increase (becomes less negative) with the increase of temperature which indicates the occurrence of exothermic process.
- (b) ΔG_{ads} may decrease (becomes more negative) with increasing temperature indicating the occurrence of endothermic process.

Therefore, the decrease of ΔG_{ads} with temperature reveals endothermic process of the corrosion inhibition of carbon steel by AYGG compound. In an endothermic process, with increasing temperature inhibitor adsorption will improve [23]. Also the positive sign of enthalpy of adsorption (ΔH_{ads}) indicates that the adsorption of inhibitor molecules is an endothermic process. The entropy of adsorption (ΔS_{ads}) in the presence of AYGG compound is positive, meaning that an increase in disordering takes places going from reactants to the metal adsorbed species reaction complex [24].

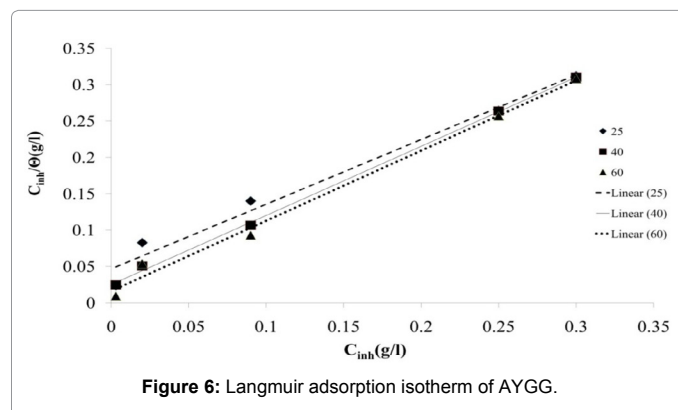


Figure 6: Langmuir adsorption isotherm of AYGG.

Temperature(°C)	K(l/g)	Slope	R ²	ΔG _{ads} (KJ/mol)	ΔH _{ads} (KJ/mol)	ΔS _{ads} (J/mol K)
25	13.17	0.84	0.85	-16.34	35.0	173
40	39.84	0.95	0.99	-20.04	35.0	173
60	61.34	0.96	0.99	-22.52	35.0	173

Table 4: Thermodynamic parameters for the adsorption of AYGG in 1 M HCl on the carbon steel at different temperatures.

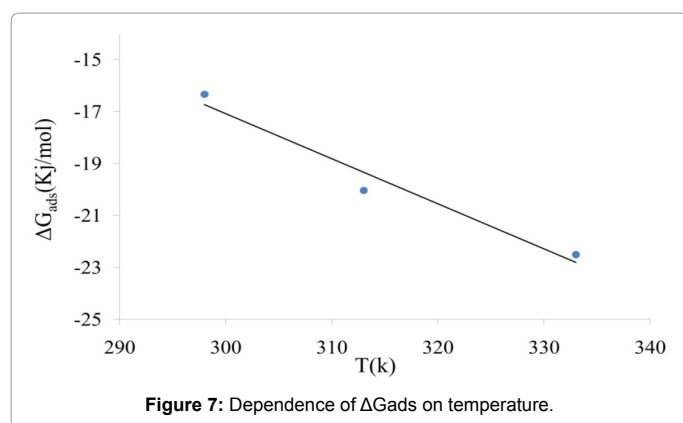


Figure 7: Dependence of ΔG_{ads} on temperature.

Activation energy

The activation energy was calculated using the integrated form of the Arrhenius equation given below:

$$\log\left(\frac{\theta_2}{\theta_1}\right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (7)$$

Where, E_a = activation energy, θ_1 and θ_2 are corrosion rates at temperatures T_1 and T_2 , respectively [25].

The average activation energy for the dissolution of carbon steel in 1 M HCl solution between 25 and 40 °C, was found to be 47.9 kJ mol⁻¹, whereas, between temperature of 40 and 60°C it was found to be 63.3 kJ mol⁻¹.

From thermodynamics point of view two types of adsorption process had been distinguished [26], physisorption in which the activation energy is less than 40 kJ mol⁻¹ and chemisorption, where activation energy is greater than 40 kJ mol⁻¹. On the basis of the experimentally determined activation energy values, the addition of this compound can be considered chemisorption adsorbed, and therefore, as the temperature raised, the adsorption of this compound on the surface of metal is improved [26,27].

Conclusions

- From the results obtained, one can conclude that AYGG is an effective corrosion inhibitor for carbon steel in HCl acid solution.
- Inhibition efficiency increased with both increase in temperature and concentration of AYGG compound.
- According to the K values, it is concluded that, the interaction between the inhibitor molecules and the metal surface is improved.

Phenomenon of chemisorption is proposed from the obtained values of kinetic and thermodynamic parameters (E_a , ΔG_{ads}), also the adsorption heat are negative values.

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