



Corrosion inhibition of carbon steel in acidic medium using azo chromotropic acid dye compound

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ABSTRACT

Corrosion inhibition effect of Azo dye compound based on chromotropic acid has been studied on carbon steel corrosion in 0.5M sulfuric acid solution using potentiodynamic polarization and weight loss techniques. The result showed that the studied azo dye is good corrosion inhibitor. The inhibition efficiency of the studied azo dye increases with increase in concentration, and decreases with increase in temperature. The morphology of the surface and the adsorption isotherm were studied. The values of thermodynamic parameters were computed and expounded.

Keywords: Chromotropic azo dyes– Corrosion– inhibitor – Carbon steel

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1. Introduction

Carbon steel is the most used kind of steel broadly. The properties of carbon steel depend mostly on the amount of carbon it contains. Most carbon steel has a carbon content of significantly less than 1%. Carbon steel is made into a variety of products, including structural beams, car bodies, appliances for kitchen, and cans. The usage of inhibitors is probably the most practical methods for corrosion protection. Various works have studied the effect of organic compounds containing nitrogen for the corrosion of carbon steel in acidic media [1–12]. These inhibitors are adsorbed on the metal surface and protect the surface of the metal from the corrosive medium. Azo dye derivatives have attracted considerable attention due to their versatile application in different fields, including cosmetic, textile, leather, food, and pharmaceutical and in high technology areas like laser, ink-jet printers and electro optical devices [13, 14]. The inhibition efficiency was set to count on physic-chemical and electronic properties of the inhibitor organic which relate to its functional groups, orbital character of donating electrons, steric effects and electronic density of donor atoms [15, 16].

This current work was designed to study the corrosion inhibition of carbon steel in 0.5M H₂SO₄ solutions by chromotropic azo dye as corrosion inhibitor using weight loss, and potentiodynamic polarization technique. Furthermore, the temperature effect on the carbon steel dissolution, as well as, on inhibition efficiency of the examined compounds was also investigated and thermodynamic parameters were computed [17, 18].

2. Experimental method

2.1. Synthesis of azo compounds

A solution of 0.01M of compound was dissolved in HCl solution (1:1) and cooled at -5°C. A 0.01 M solution of sodium nitrite was prepared separately and kept cooled at -

5°C. The cooled nitrite solution was gradually added to the amine solution with continuous stirring and the temperature kept at -5°C. A 0.01 M solution of chromotropic acid disodium salt was prepared by dissolving the appropriate amount of the solid acid in 10% NaOH, the coupler solution was cooled at -5°C. The diazonium salt solution was coupled with the chromotropic acid solution. After dilution the crude azo dye was collected by filtration and crystallized from petroleum ether (40:60), then dried in vacuum desiccator over anhydrous CaCl₂. structural formula is represented in Fig 1.

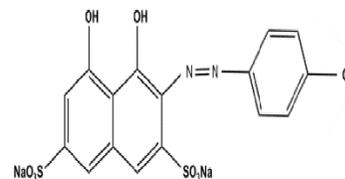


Fig (1): structural formula of the azo dye

2.2. Weight loss measurements

The steel sample used had the composition (wt. %) 0.11 C, 0.10 Si, 0.69Mn, 0.038 P, 0.019 S, 0.05 Cr, 0.09Ni, 0.04Cu and the remainder Fe. Pieces of steel with dimension of 1.5 x 2 x 0.1 cm were used for weight loss measurements. The electrode surface was polished with different grades of emery paper, degreased with acetone, and rinsed with distilled water. The cleaned C-steel pieces were weighed before and after immersion in 50 ml of the test solution for a period of time 4 hr. The weight loss for each sample was taken and expressed in mg cm⁻². The required temperature was adjusted using water bath thermostat.

2.3. Potentiodynamic polarization measurements

The electrochemical tests were performed in a conventional three-electrode electrochemical cell at 30°C, consisting of carbon steel electrode with an exposed area of 2 cm² as working electrode, a saturated calomel electrode as reference electrode, and a platinum sheet as counter electrode were used for electrochemical studies. Potentiodynamic polarization experiments were carried out using a PS remote potentiostat with PS6 software at scan rate 10 mV/sec.

2.4. SEM measurements

The steel pieces were polished using different grades of emery paper up to 2000 grit size then keeping for 4hrs. in 0.5 M sulfuric acid solution without and with 0.02 M of inhibitor. After this immersion time, the specimen was washed gently with distilled water, then carefully dried and put into the spectrometer without any further treatment.

3. Results and discussion

3.1. Weight loss measurements

The weight loss of steel specimen in uninhibited acid solution and solutions containing different concentrations of the inhibitor was determined after 4h immersion and listed in Table 1. The corrosion rate (CR), inhibition efficiency (%IE) and surface coverage (θ) was obtained from weight loss measurements were calculated and given in Table 1 using the following equations:

$$CR = (w-w_0) / S t \tag{7}$$

$$\%IE = [1 - \frac{w}{w_0}] \times 100 \tag{8}$$

$$\theta = [1 - \frac{w}{w_0}] \tag{9}$$

Where w and w₀ are weight losses in the absence and presence of inhibitor, respectively, S is the surface area (cm²), and t is the exposed time (hr.)

These results showed that, as the inhibitor concentration increases, the weight loss and corrosion rate decreases while, the inhibition efficiency increases. It may be concluded that the inhibitor act through adsorption on surface of metal and formation of a barrier layer between metal and corrosive media.

Table (1): Corrosion rate, inhibition efficiency and surface coverage of azo dye compound for corrosion of C-steel in 0.5M H₂SO₄ solutions using weight loss method at 30°C.

Inhibitor	concentration	Wt. Loss gm	CR gm.cm ⁻² .hr ⁻¹	%I.E	θ
Azo compound	3x10 ⁻³	0.18	0.0112	21.7	0.217
	7x10 ⁻³	0.12	0.0075	47.8	0.478
	9x10 ⁻³	0.11	0.0068	52.1	0.521
	1x10 ⁻²	0.07	0.0043	69.5	0.695
	2x10 ⁻²	0.04	0.0025	82.3	0.823

3.2. Adsorption isotherm

In order to confirm the adsorption of the investigated inhibitor on metal surface, the adsorption isotherms were studied. The adsorption isotherms can provide basic information on the interaction of inhibitor with metal surface. The surface coverage (θ) values, for different concentrations of the azo compound in 0.5M H₂SO₄ solution have been obtained from weight loss measurements and examined graphically for fitting of appropriate adsorption isotherm. The plot of θ versus log C (Fig.3) yields a straight line indicated that the adsorption of the compound from sulfuric acid solution on mild steel surface obeys the Temkin adsorption isotherm presented in the following equation: [21]

$$\theta = (1/a) \ln KC \tag{10}$$

Where C is the inhibitor concentration, K is the equilibrium constant for adsorption reaction in the bulk of the solution and a is the molecule interaction parameters depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface of the metal. The plot of θ against log C give straight line, as

shown in Fig.2, which indicates that the compound is adsorbed on the surface of C-steel electrode according to Temkin adsorption isotherm. From the slope values of these plots, the equilibrium constant values were calculated and given in Table 2.

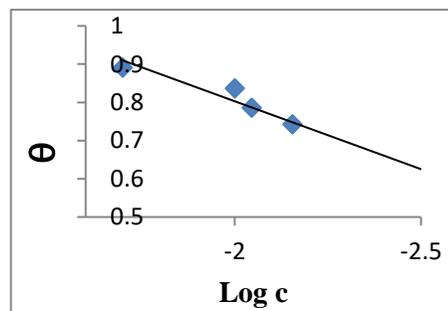


Fig (2): Temkin adsorption isotherm plotted as θ vs. log C of the investigated inhibitor for corrosion of carbon steel in 0.5M H₂SO₄ solution from weight loss method at 30°C.

The relation between the equilibrium constant and the standard free energy of adsorption is given by the following equation [19, 20]:

$$K=1/55.5 \exp (- \Delta G^{\circ}_{\text{ads}} /RT) \tag{11}$$

Where T is the absolute temperature, R is the gas constant (8.314 J. mol⁻¹.k⁻¹) and the numerical value 55.5 is the concentration of water in mol.L⁻¹.

The values of the free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) were calculated and represented in Table (2), This negative value of $\Delta G^{\circ}_{\text{ads}}$ denotes that the adsorption process is spontaneous. The calculated values of $\Delta G^{\circ}_{\text{ads}}$ are greater than -20 kJ mol⁻¹ but less than - 40 kJ mol⁻¹, indicating that the adsorption of azo dyes on carbon steel in 0.5M H₂SO₄ solution may be a combination of both physisorption and chemisorption [22].

Table (2): The Temkin adsorption isotherm parameters

Inhibitor	R ²	Log K	A	$\Delta G^{\circ}_{\text{ads}}$ kJ.mol ⁻¹
Azo compound	0.971	2.88	-0.66	-27.4

3.3. Potentiodynamic polarization measurements

Fig.3 shows typical anodic and cathodic polarization curves of carbon steel in 0.5M H₂SO₄ in absence and presence of varying concentrations of inhibitor.

The values of cathodic (β_c) and anodic (β_a) Tafel constants were, calculated from the linear region of the curves of polarization. The corrosion current density (I_{corr}) was specified from the intersection of the linear part of cathodic, and anodic curves with stationary corrosion potential (E_{corr}).

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

$$\% \text{IE} = [1 - I_{\text{add}} / I_{\text{free}}] \times 100 \tag{12}$$

Where I_{add} and I_{free} are the corrosion current densities in the presence and absence of inhibitor, respectively. The obtained corrosion parameters are represented in Table3.

The inhibition efficiency increased by increasing the inhibitor concentration, indicating the compound retard the dissolution of C-steel in 0.5M H₂SO₄ solution and the degree of inhibition depends on the concentration and type of the inhibitor. This implies that the compound was acting as good inhibitor. The corrosion potential (E_{corr}), the cathodic and anodic Tafel lines does not remarkably shifted in presence of these investigated compound, therefore the compound can be described as mixed type inhibitor for C-steel in 0.5M H₂SO₄ solution [23].

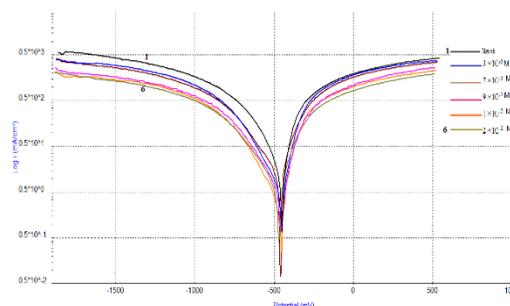


Fig (3): Potentiodynamic polarization curves for the dissolution of carbon steel in 0.5 M H₂SO₄ in absence and presence of different concentrations of azo compound at 30°C.

Table (3):The values of corrosion parameters for the corrosion of carbon steel in 0.5M of H₂SO₄ by potentiodynamic polarization technique.

Inhibitor	Conc. M	I corr (mAcm ⁻²)	-E corr mV	β_a mV dec ⁻¹	$-\beta_c$ mV dec ⁻¹	%IE	θ
Blank	-	3.61	462	102.4	153.1	-	-
Azo compound	3×10^{-3}	1.23	452	85.6	163.6	65.9	0.659
	7×10^{-3}	1.22	495	112.7	202.1	66.2	0.662
	9×10^{-3}	1.09	484	114.5	183.2	69.8	0.698
	1×10^{-2}	1.02	474	99.8	184.7	71.7	0.717
	2×10^{-2}	0.97	458	92.5	179.1	73.1	0.731

3.4. The temperature effect

The influence of rising temperature on the corrosion rate of C-steel in 0.5 M H₂SO₄ in the presence of highest concentration of the azo dye compound (2×10^{-2} M) was studied using weight loss measurements. The corrosion rate (CR) and the inhibition efficiency (IE) were calculated at different temperatures (303° k, 313° k, 323° k, 333°k and 343° k), according to Fig.5 the %IE values were plotted verses the temperature and %IE decreases as the temperature increases. This indicates that the rising of

temperature decreases the inhibition process, and the highest inhibition efficiency is obtained at the lowest temperature. The decrease of %IE on increasing temperature is attributed to an appreciable decrease in the adsorption process of the inhibitor on the metal surface and the corresponding increase of the reaction rate.

The values of activation energy E_a of the corrosion process in absence and presence of the highest concentration of inhibitors were calculated using Arrhenius equation [24, 25]:

$$\text{Log CR} = \log A - E_a / 2.303 RT \quad (13)$$

Where CR is the rate of corrosion from weight loss, A is Arrhenius constant, R is the gas constant and T is absolute temperature.

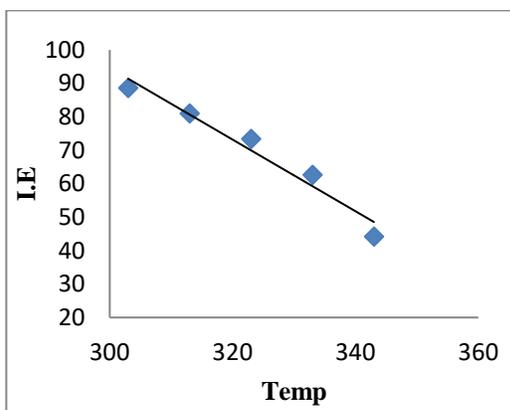


Fig (4): Variation of inhibition efficiency with temperature at the highest concentration ($2 \times 10^{-2} \text{M}$) for the corrosion of carbon steel in $0.5 \text{M H}_2\text{SO}_4$ of azo compound.

Fig.5 represents Arrhenius plot ($\log R_{\text{corr}}$ vs. $1/T$) for the azo compound. From the slopes of the plot, the activation energy value was calculated and represented in Table 4.

The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the azo compound was calculated using the transition state equation [26]:

$$\log \left(\frac{CR}{T} \right) = \left[\left(\log \frac{R}{hN} \right) + \left(\frac{\Delta S}{2.303RT} \right) \right] - \left(\frac{\Delta H}{2.303RT} \right) \quad (14)$$

Where, h is Plank’s constant ($6.62606957 \times 10^{-34} \text{J}\cdot\text{sec}$), N is Avogadro’s number ($6.02214129 \times 10^{23} \text{mol}^{-1}$).

Fig. 6 shows the plots of $\log \left(\frac{CR}{T} \right)$ against $\left(\frac{1}{T} \right)$. For the azo compound, straight lines were obtained with slope of $\left(-\frac{\Delta H}{2.303R} \right)$ and an intercept of $\left(\log \frac{R}{hN} \right) + \left(\frac{\Delta S}{2.303R} \right)$, the calculated value of the apparent activation enthalpy ΔH^* , and activation ΔS^* , are given in Table 4.

Inspection of data of Table 4 reveals that the activation enthalpy for the inhibited solution, the ΔH^* value is higher than the uninhibited solution. The positive sign of activation enthalpy (ΔH^*) reflect the endothermic nature of dissolution process [27].The value of entropy of activation ΔS^* in tested solution is negative.

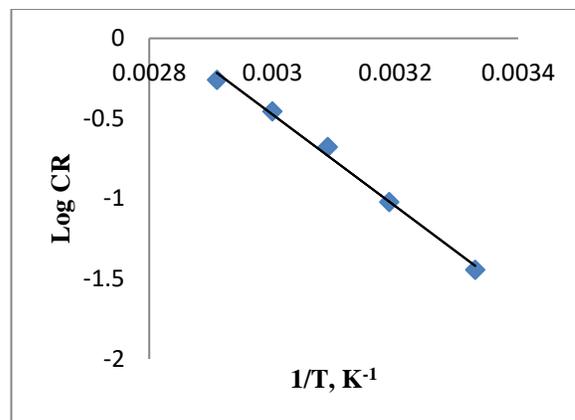


Fig (5):Arrhenius plots ($\log CR$ vs $1/T$) for the corrosion of carbon steel in $0.5 \text{M H}_2\text{SO}_4$ at the highest concentration ($2 \times 10^{-2} \text{M}$) of azo compound.

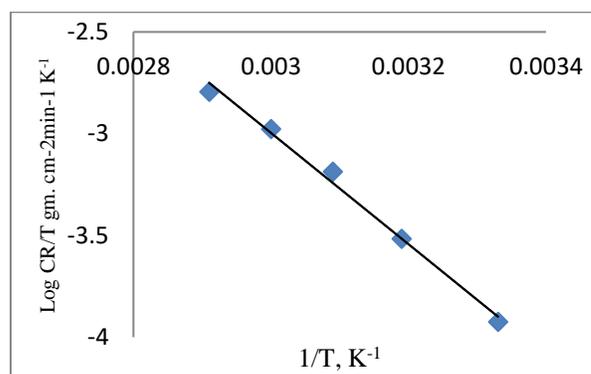


Fig (6): plots ($\log CR/T$ vs $1/T$) for the corrosion of carbon steel in $0.5 \text{M H}_2\text{SO}_4$ at the highest concentration ($2 \times 10^{-2} \text{M}$) of azo compound.

Table (4): Activation parameters for the dissolution of C-steel in $0.5 \text{M H}_2\text{SO}_4$.

Inhibitor	E_a KJ mol ⁻¹	ΔH^* KJ mol ⁻¹	ΔS^* J mol ⁻¹ K ⁻¹
Blank	24.7993	22.3159	-180.01
Azo compound	51.6436	51.6494	-97.806

3.5. Study the surface morphology

Fig.7 represents the SEM obtained of carbon steel samples after immersion in $0.5 \text{M H}_2\text{SO}_4$ in absence and presence of 0.02M inhibitor for 4 hours. It is clear that carbon steel surfaces in the absence of the inhibitor are strongly damaged. While the morphology of carbon steel surface in presence of inhibitor is quite different from the previous one, the specimen surface was smoother.

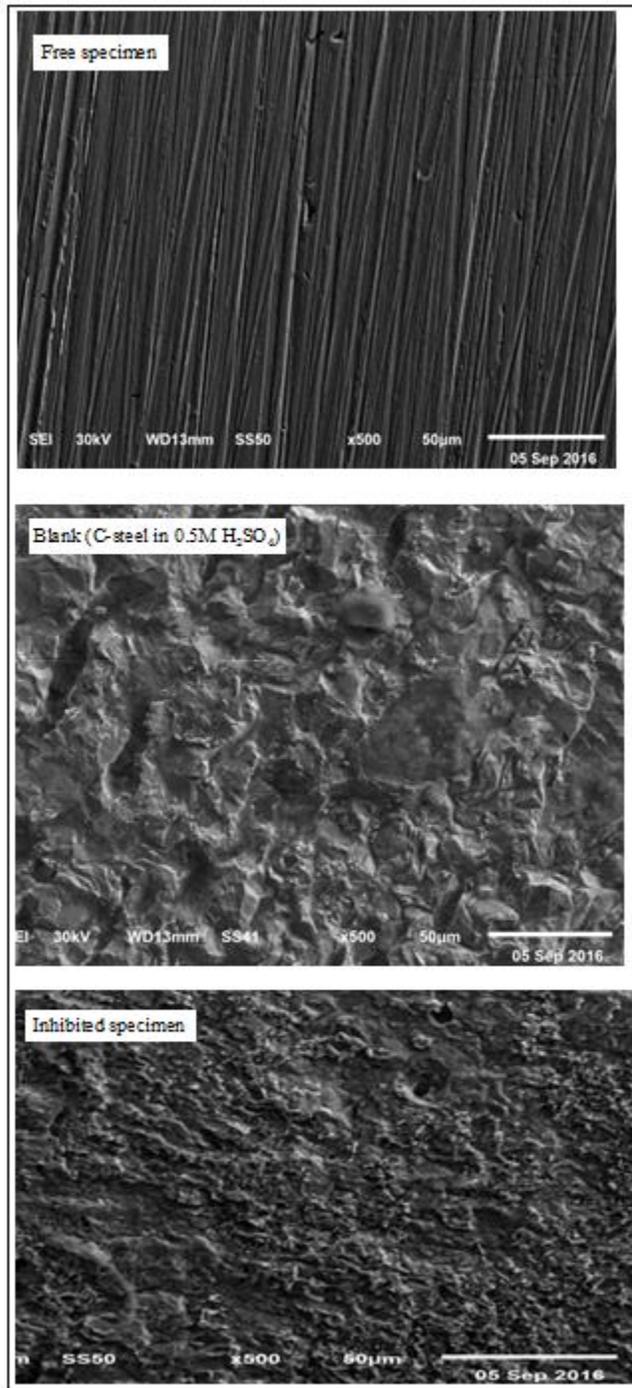


Fig (7): SEM micrographs for C-steel in absence and presence of inhibitor.

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