Azoisonicotinohydrazide derivative as carbon steel corrosion inhibitor in 1 M H₂SO₄: potentiostatic, adsorption isotherm and surface studies

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Abstract

The inhibition of carbon steel corrosion in acidic media (1 M, H₂SO₄) by the new hydrazone derivative, namely N'-((E)-2-hydroxy-5-((E)-phenyldiazenyl)benzylidene)isonicotinohydrazide (AS), in combination with nonionic surfactant (Tween 80) have been investigated by electrochemical method (potentiostatic polarization) and surface analyses (scanning electron microscopy). The obtained results confirmed that the new compound (AS) acts as good carbon steel corrosion inhibitor in 1 M H₂SO₄. The effect of both concentration of AS and temperature have been studied. The highest recorded inhibition efficiency was 91.02% in the presence of 0.08 mM of AS at 323 K. The studied compound AS was effectively adsorbed on the carbon steel surface and the adsorption process obeys the Langmuir isotherms model with correlation coefficient around 0.92. The adsorption studies proved that the adsorption process is mixed type adsorption, spontaneous and exothermic process. The potentiostatic results indicated that the new corrosion inhibitor (AS) is a mixed type inhibitor with predominant anodic effect. The scanning electron microscope analyses confirmed the good performance of the used corrosion inhibitor (AS), the severe damage of the carbon steel specimen surface caused by the aggressive attack of the acid solution was found to be significantly reduced when treated with the acidic solution in the presence of AS.

Keywords: corrosion, carbon steel, organic inhibitors, adsorption.

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Introduction

Corrosion is a serious problem that happens to metallic resources when treated with acidic solutions such as H_2SO_4 and HCl solutions for different purposes such as pickling, oil acidification and descaling, therefore it is necessary control the dissolution of metals and minimize the damage caused by corrosion [1, 2].

The use of organic additives to the acidic solutions is one of the implemented procedures to control the corrosion process as they act as corrosion inhibitors [3]. The usually used organic compounds contain delocalized π electron, hetero atoms (such as N,

O, S and P) and polar functional groups (such as NO_2 , -SH, -CN, $-NH_2$, -OH *etc.*) in their molecular structures [4–6]. The presence of these atoms and functional groups as adsorption centers makes the inhibitors readily adsorbed on the metal surface forming layers that protect the metal from the aggressive acidic attack (inhibiting the corrosion) [7–10]. Researchers are continuing their endeavors in this field focusing on the development of new organic inhibitors which are cost effective, readily synthesized, have good solubility, low toxicity and high corrosion inhibition efficiency [11, 12].

As a part of our interests [13, 14], herein we report the use of a hydrazone (AS) as a new carbon steel corrosion inhibitor in combination with a nonionic surfactant (Tween 80) as an eco-friendly carbon steel corrosion inhibitor with high inhibition efficiency at low concentration in $1 \text{ M H}_2\text{SO}_4$.

Experimental

Specimens preparation

A rod of carbon steel contain the following ratio of elements (0.07% C, 0.16 % Si, 0.24 % Mn, 0.0005 % p, 0.16 % S, 0.04 % Cr,0.005 % Mo, 0.06% Ni, 0.008 % Al, 0.12% Cu and Fe) was cut into cylindrical shape (24 mm diameter and 3 mm height), surface was then ground and polished with different grades of emery paper (220–3000) and polishing paste (diamond suspension, 3 μ m) by using a mechanical machine, and kept in a desiccator.

Synthesis of AS

Compound (AS) was synthesized according to a literature procedure as illustrated in Scheme 1 [[15:



Scheme 1. Synthesis of AS.

Solutions preparation

Different concentrations of AS were prepared (0.02, 0.04, 0.06 and 0.08 mM) by dissolving the appropriate weight in H_2SO_4 solution (1000 ml, 1 M, and 2 ml, DMSO), Tween-80 (0.01g) has been added to get a clear solution.

Potentiostatic polarization measurements

The potentiostatic polarization measurements were performed by using three electrodes cell: saturated calomel electrode Hg/Hg₂Cl₂ (reference electrode), Pt electrode (auxiliary electrode) and the studied specimen (working electrode). The working electrode was immersed in the test solution (in presence and absence AS) for 30 min and time step 1 sec until attain open circuit potential (OCP). The applied constant sweep rate was 0.3 mV s⁻¹ and the changing in electrode potentials was ± 250 mV [16]. By extrapolating the linear segments of Tafel slopes: the corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined. The I_{corr} values were used to calculate the inhibition efficiency according to equation (1) [17].

$$\eta\% = \frac{I_{\rm corr} - I_{\rm inh}}{I_{\rm corr}} \times 100 \tag{1}$$

where I_{corr} and I_{inh} refers to corrosion current densities without and with AS respectively.

Surface analysis

A carbon steel specimen was immersed in the acid solution (1 M H_2SO_4) in absence and presence of AS (0.08 mM) at 323 K for 3 hours, then, washed by absolute ethanol, dried and tested by scanning electron microscope (SEM, Quanta 450 FEI, voltage 25 kV, spot size 3.5 mm).

Results

Potentiostatic polarization measurement

The potentiostatic polarization technique has been used to study the effect of the presence of deferent concentrations of AS on the corrosion of carbon steel in 1 M H₂SO₄ over the range of temperatures 303–333 K. Figure 1 furnishes the generated Tafel curves, the obtained polarization parameters including corrosion potential (E_{corr}), corrosion current density (I_{corr}), slopes of the linear segments anodic (β_a) and cathodic (β_c) Tafel slopes, inhibition efficiency (η %) and surface coverage (θ) are shown in Table 1. The shifts of both anodic and cathodic curves branches toward lower current densities indicate that AS behaves as corrosion inhibitor [18], the decrement in the current densities with increasing the concentration of AS explain that increasing the concentration leads to increasing the corrosion inhibition efficiency at each certain temperature, the inhibition efficiency was found to be increasing with elevating the temperature within the range 303–323 K and then drop down at 333 K, the highest corrosion inhibition efficiency (91.02%) was recorded in the presence of 0.08 mM of AS at 323 K in 1 M H₂SO₄.

The inhibitor can be classified as cathodic, anodic or mixed type inhibitor according to its effect on the electrode reaction, anodic when it interrupts the anodic reaction (carbon steel dissolution reaction), cathodic when it interrupts the cathode reaction (H^+ reduction) and mixed type inhibitor when it interrupts both of them [19].

In this study we found that AS is a mixed type inhibitor with predominate anodic effect, since it interrupts the both electrochemical reactions [20]. Figure 1 shows the shifts in both curve branches. Table 1 shows that anodic (β_a) and cathodic (β_c) Tafel slopes are changed at the same time with different concentrations of AS [21]. The maximum displacement in E_{corr} values was less than 85 mV (41 mV) with respect to the E_{corr} of the blank solution (the acid solution with only Tween-80 added in the same concentration used in the test samples), this is another evidence that AS inhibitor is mixed type inhibitor [22]. In addition the positive shift (noble direction) of corrosion potential in the presence of AS at constant temperature, gives an evidence that AS is obstructing the anodic reaction (blocking the available active sites on the metal surface) [23].



Figure 1. Potentiostatic polarization curves for carbon steel in $1 \text{ M H}_2\text{SO}_4$ in the absence and presence of AS over temperature range 303–333 K.

Conc. mM	Temp. K	-E _{corr} (mV)	I _{corr} (μA/cm ²)	$\beta_a \ (mV \ dec^{-1})$	$-\beta_c (mV \ dec^{-1})$	η%	θ
Blank		442.4	1120.0	54.3	74.4	0	0
0.02		412.0	487.10	35.7	93.9	58.30	0.58
0.04	303	416.6	313.69	37.6	99.7	71.99	0.71
0.06		408.3	297.09	42.1	103.0	73.74	0.73
0.08		408.9	250.10	23.5	56.2	77.60	0.77
Blank		446.0	1520.0	58.8	62.4	0	0
0.02		400.3	574.63	31.6	66.3	63.97	0.63
0.04	313	401.7	411.59	35.4	77.8	72.92	0.72
0.06		388.3	346.72	24.2	58.7	77.18	0.77
0.08		405.3	268.28	32.8	78.6	82.30	0.82
Blank		439.2	3630.0	76.5	65.0	0	0
0.02		409.0	1200.0	42.5	66.3	66.94	0.66
0.04	323	388.1	705.56	38.2	77.8	80.56	0.80
0.06		384.4	524.83	39.8	58.7	85.65	0.85
0.08		404.9	325.49	37.6	78.6	91.02	0.91
Blank		433.9	5390	89.2	71.3	0	0
0.02		400.6	2190	56.2	70.5	59.36	0.59
0.04	333	383.3	1190	37.8	49.4	77.92	0.77
0.06		382.2	922.66	38.7	56.4	82.88	0.82
0.08		389.1	815.79	38.8	104.5	84.86	0.84

Table 1. Polarization parameters for carbon steel corrosion in $1 \text{ M H}_2\text{SO}_4$ in the presence of different concentrations AS at different temperatures.

Adsorption isotherms

The adsorption isotherms for the AS on the carbon steel alloy were studied to give more information about the nature of interaction between the metal surface and the inhibitor molecules (AS). The experimental outcomes form the potentiostatic polarization studies are used to test several adsorption isotherms, and the best fitting was found obey Langmuir isotherms model. The adsorption constants (K_{ads}) were calculated according to Langmuir equation (2), Figure 2 shows the Langmuir relationship for adsorption of AS inhibitor in 1 M H₂SO₄ acid over the temperature range 303–333 K.

The Gibbs free energy of the adsorption process (ΔG_{ads}) was calculated according to equation (3), then logarithm of K_{ads} values were plotted against 1/*T* (Figure 3) according to equation (4) to calculate the reaction enthalpy ΔH_{ads} [24, 25].

$$\frac{C_{\rm inh}}{\theta} = \frac{1}{K_{\rm ads}} + C \tag{2}$$

$$\Delta G_{\rm ads} = -RT \ln \left(55.5 \, K_{\rm ads} \right) \tag{3}$$

$$\log K_{\rm ads} = \left(-\frac{\Delta H_{\rm ads}}{2.303 RT}\right) + Constant \tag{4}$$

Where C_{inh} is concentration of the inhibitor, θ is the surface coverage, *T* is the absolute temperature and *R* is the universal gas constant. The numerical value of 55.5 represents the molar concentration of water in acid solution.

In which the surface coverage was calculated according to equation (5) [26]:

$$\theta = \frac{\eta\%}{100} \tag{5}$$

Table 2 shows the results obtained for the adsorption studies, the negative ΔG_{ads} value which $-33.21 \text{ kJ} \cdot \text{mol}^{-1}$ tells that the interaction between the molecules of AS and metal surface is mixed adsorption (both physisorption and chemisorption), accordingly we assume that the molecules of AS block the corrosion sites and prevent the reaction between the acid and metal surface (inhibits the metal dissolution), the calculations involved in this study are based on this assumption [27]. The negative value of enthalpy (ΔH_{ads}) refers to the exothermic adsorption, its value (<40 kJ·mol⁻¹) is a furthermore indicator of the mixed type nature of adsorption process [28]. The calculated values of ΔS_{ads} indicates that the process is progressing toward the more ordered system [29].



Figure 2. Langmuir relationship for adsorption of AS inhibitor in 1 M H₂SO₄ acid over temperature range 303–333 K.



Figure 3. Log K_{ads} versus 1/T for carbon steel with and without AS inhibitor in 1 M sulfuric acid solution over temperature range 303–333 K.

Compound symbol	Medium Conc./M	Temp. K	$K_{ m ads} \ { m M}^{-1}$	$\Delta G_{ m ads} \ { m kJ}{ m \cdot mol}^{-1}$	$\Delta H_{ m ads} \ { m kJ} \cdot { m mol}^{-1}$	$\frac{\Delta S_{\rm ads}}{\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1}}$
		303	45.045		-19.7099	-33.1450
	1 14	313	23.1481	-33.21	-18.6279	-33.1505
AS	1 M	323	17.8253		-18.5214	-33.1527
		333	13.2275		-18.2689	-33.1551

Table 2. The calculated thermodynamic parameters for the adsorption of AS.

Surface analysis

Scanning electron microscopy (SEM) has been used test the morphology of the carbon steel surface after exposure to the aggressive acidic solution $(1 \text{ M H}_2\text{SO}_4)$ in the absence and presence of AS (0.08 mM at 323 K) for 3 hours, the SEM micrographs of the corroded specimen. Figure 4 (a) shows the huge damage caused by the effect of the acidic corrosion, on the other hand SEM micrographs of the inhibited specimen, Figure 4 (b) explains how the damaging effect of the acid has been reduced to the minimum in the presence of AS, adding more evidence that it is an excellent carbon steel corrosion inhibitor.

Conclusions

The azoisonicotinohydrazide derivative (AS) in combination with Tween 80 is acting as an excellent carbon steel corrosion inhibitor; it has high corrosion inhibition efficiency at relatively low molar concentration.



Figure 4. SEM micrographs of corroded (a) and inhibited with AS (b) carbon steel surfaces.

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