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Inhibition of Mild Steel Corrosion by Purpald in Highly Sulfuric Acid Solution

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The inhibition of mild steel corrosion in 2.5M H_2SO_4 solution by purpald (4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole, 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol) at 30 °C was investigated by means of electrochemical polarization and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization results were comparable with those obtained by impedance measurements. Results showed that purpald performed excellent as inhibitor for mild steel corrosion in 2.5M H_2SO_4 solution and it attains an efficiency of more than 95% at 4×10^{-4} M at 30 °C . The inhibition efficiency increases with an increase in the concentration of purpald. Polarization curves show that purpald is a mix-type inhibitor. Changes in impedance parameters (charge transfer resistance, R_{ct}, and double layer capacitance, C_{dl}) were indicative of adsorption of purpald on the mild steel surface, leading to the formation of protective films.

Keywords: Corrosion inhibition, acidic corrosion, mild steel, EIS

1. INTRODUCTION

The use of acid solution during pickling and industrial cleaning leads to corrosive attack on mild steel. The corrosion of mild steel is of fundamental academic and industrial concern that has received a considerable amount of attention. The protection of mild steel against corrosion can be achieved by adding organic compounds in small concentrations to environment [1, 2]. A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. Compounds studied as inhibitors include triazole derivatives [3], bipyrazolic derivatives [4], surfactants [5] aromatic hydrazides [6], organic dyes [7], Poly (4-vinylpyridine) [8] and thiosemicarbazide-type organic compounds [9]. These compounds can adsorb on the mild steel surface and block the active sites decreasing the corrosion rate.

The aim of the present study was to examine the inhibitive action of purpald (4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole, 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol) towards the corrosion of mild steel in 2.5M H_2SO_4 solution.

2. EXPERIMENTAL

Commercially mild steel metal was used as working electrode. Mild steel sample was mechanically polished using SiC paper in successive grades from 250 to 1500 and was rinsed with methanol. The molecular structure of the investigated organic compound is shown in Fig. 1. The acid solutions were made from RA grade H_2SO_4. Appropriate concentration of acid was prepared by using distilled water. The measurements were carried out in a three electrodes electrochemical cell with a graphite counter electrode and saturated calomel electrode (SCE) as reference. Tafel polarization curves were obtained starting from E_{corr} with the potential scan rate of 0.5 mVs^{-1}. EIS measurement was carried out on steady state open circuit potential (OCP) disturbed with amplitude of 5 mV A.C. sine wave at frequencies between 0. 1 Hz and 10 KHz. Measurements were performed at room temperature using Gamery instrument Ref600 Potentiostat/Galvanostat/ZRA.

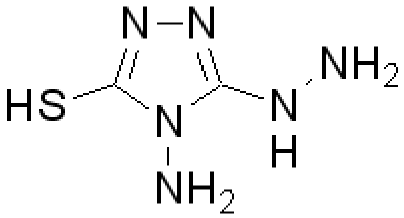

Figure 1. molecular structure for purpald.

3. RESULTS AND DISCUSSION

3.1. Polarization measurements

The effect of the concentration of purpald is shown in Fig.2 which presents the anodic and cathodic Tafel curves of mild steel in 2.5 M H_2SO_4. Values of anodic β_a and cathodic β_c Tafel constant and corrosion current density are listed in Table 1. These values were calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at $E_{corr.}$ The inhibition efficiencies are calculated by the following expression:

$$IE\% = \frac{i_{uninhibit} - i_{inhibit}}{i_{uninhibit}} \times 100 \qquad (1)$$

where $i_{uninhibit}$ and $i_{inhibit}$ are respectively, the corrosion current density without and with purpald in 2.5 M H_2SO_4 solution.

The anodic and cathodic Tafel lines for mild steel in presence of purpald were almost parallel upon increasing inhibitor concentrations. This suggests that the inhibitor act by simple blocking the mild steel surface [10]. In the other words, the inhibitor decreasing the exposed surface area for corrosion as well as it doesn't affect the mechanism of mild steel dissolution or hydrogen evolution reaction. Only when the change in E_{corr} value is no less than 85 mV, a compound can be recognized as an anodic or a cathodic type inhibitor [1]. The largest displacement of the corrosion potentials (E) were about 29 mV in presence of purpald. Therefore, purpald is acts as corrosion mixed-type inhibitors. Also the inhibition efficiencies increase with increasing inhibitors concentration.

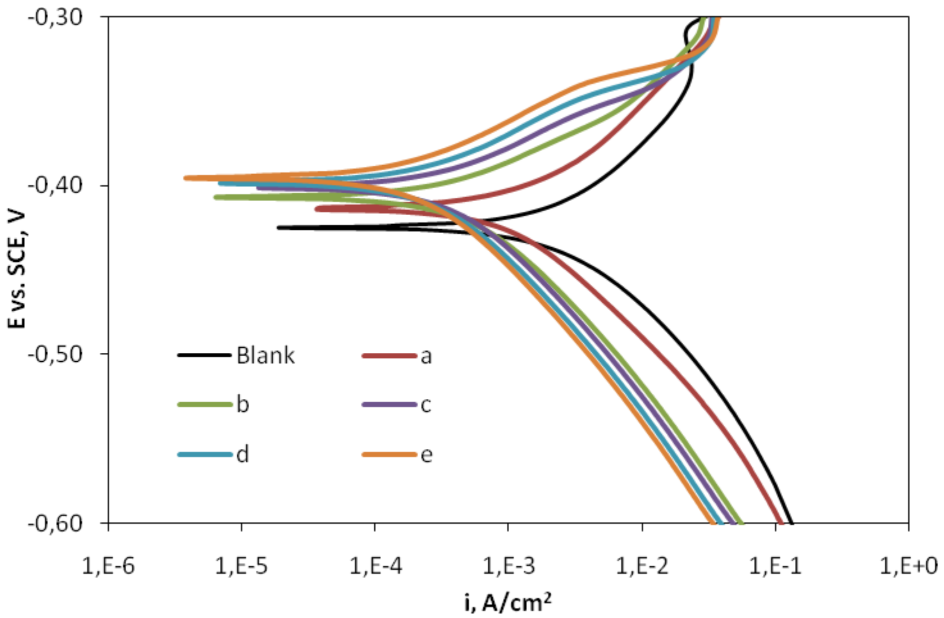

Figure 2. Polarization curves for mild steel in 2.5 M H_2SO_4 at 30 °C in absence and presence of various concentrations of purpald: (a) 0.5, (b) 1, (c) 2, (d) 3, (e) 4 $\times 10^{-4}$ M.

3.2. EIS measurements

The results of EIS were figured by Nyquist plots, Fig 3. In the impedance spectra of mild steel in the presence of purpald, the Nyquist plot has one loop in the high frequency region (HF) and at intermediate frequency (MF). This attributed to the to the charge-transfer process. The corroding surface of mild steel in 2.5 M H_2SO_4 is expected to be inhomogeneous because of its roughness; therefore, the capacitance is presented through a constant phase element (CPE).

Figures 4 represent the equivalent circuit design used to fit the experimental EIS data for sulfuric acid in the absence and presence of inhibitor, respectively [1]. The circuit elements for the data obtained include a solution resistance, R_s, a constant phase element, CPE_{dl}, and a charge-transfer resistance, R_{ct} the value of R_{ct} is indicative of electron transfer across the interface.

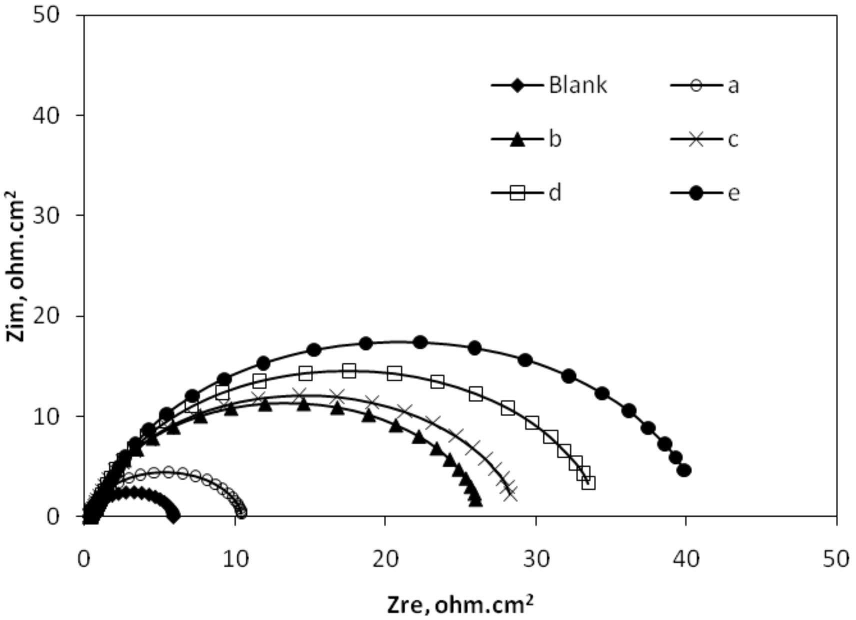

Figure 3. Nyquist plots for mild steel in 2.5 M H_2SO_4 at 30 °C in absence and presence of various concentrations of purpald: (a) 0.5, (b) 1, (c) 2, (d) 3, (e) 4 $\times 10^{-4}$ M.

The fitted values of R_{ct} and CPE_{dl} , and n are listed in Table 1. CPE is defined in impedance representation as [1]:

$$Z(\omega) = Y_0 \cdot (j\omega)^{-n} \quad (2)$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad/s), $j^2 = -1$ is an imaginary number, and n is the CPE exponent.

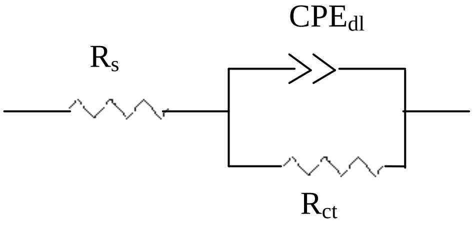

Figure 4. The equivalent circuit model used to fit the impedance data for mild steel in the absence and presence of purpald. R_s = solution resistance, R_{ct} = charge-transfer resistance, CPE_{dl} = constant phase element of the double layer.

In order to confirm the polarization results, the inhibition efficiencies (*IE%*) at different concentrations of purpald in a 2.5 M H_2SO_4 solution were also calculated from the corresponding electrochemical impedance data according to Eq. (3) [1]:

$$IE\% = \frac{R_{ct} - R^{\circ}_{ct}}{R_{ct}} \times 100 \qquad (3)$$

where R_{ct} and R°_{ct} are the charge-transfer resistance with and without purpald, respectively. Table 1 show that the charge-transfer resistances, R_{ct}, increased with increasing concentrations of purpald while C_{dl} tend to decrease.

Table 1. Polarization and EIS parameters for mild steel in 2.5 M H_2SO_4 with different concentrations of purpald.

Technique	Parameters	Inhibitor concentration (M) $\times 10^{-4}$					
		Blank	0.5	1	2	3	4
Polarization parameters	E_{corr} (mV)	424	413	406	401	397	395
	i_{corr} (µA/cm^2)	5050	1880	681	426	322	267
	β_a (V/decade)	0.13	0.09	0.06	0.04	0.04	0.05
	β_c (V/decade)	0.12	0.1	0.09	0.09	0.09	0.09
	θ		0.63	0.87	0.92	0.94	0.95
	IE%		63	87	92	94	95
EIS parameters	R_{ct} (ohm. cm^2)	5.5	9.9	25.8	28.7	35	42.4
	R_s(ohm. cm^2)	0.29	0.27	0.36	0.33	0.4	0.42
	CPE_{dl}, $Y_0 \times 10^{-6}$ ohm^{-1}cm^{-2} S^n	774	692	600	726	842	852
	n	0.97	0.96	0.92	0.89	0.86	0.85
	C_{dl} (µF/cm^2)	635	562	418	450	474	474
	IE%		44	79	81	84	87

This suggests that the purpald molecules are adsorbed on the mild steel surface, to protect its surface from acid corrosion. The decrease in n values with purpald concentration revealed that the adsorbed film become more uneven. The R_{ct} values increase with the increase in concentration of purpald, indicating an insulated adsorption layer's formation. This result followed the same general trend of the *IE%* obtained from the potentiodynamic polarization measurement.

3.3. Temperature effect

The mechanism of the inhibitor action can be deduced by comparing the apparent activation energies, E_a, in the presence and absence of the corrosion inhibitor. Activation parameters such as E_a, the enthalpy of activation, ΔH_a, and the entropy of activation, ΔS_a, for both corrosion and corrosion inhibition of mild steel in 2.5 M H_2SO_4 in the absence and presence of 0.4 mM concentration of purpald in the range of temperatures (30 to 60 °C) were calculated from an Arrhenius-type plot (eq. 4) and transition state (eq. 5), respectively. Figures 5and 6 represent the data plots of ln(i_{corr}) versus

$1000/T$ and $\ln(i_{corr}/T)$ versus $1000/T$, respectively, in the absence and presence of 0.4 mM concentration of the purpald. The calculated values of E_a, ΔH_a and ΔS_a are tabulated in Table 2.

$$\mathrm{Log}\ i_{corr} = \log(A) - \frac{E_a}{2.303RT} \tag{4}$$

$$\ln\left(\frac{i_{corr}}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

Table 2. Corrosion kinetic parameters for mild steel in 2.5 M H_2SO_4 in the absence and presence of 0.4 mM concentration of purpald.

	E_a, kJ mol^{-1}	ΔH_a, kJ mol^{-1}	ΔS_a, J mol^{-1} K^{-1}
Blank	30.96	28.32	-196.30
Blank+ purpald	97.32	94.67	-0.50

The results show that the apparent activation energies increase with the presence of purpald, which indicated physical adsorption (electrostatic) in the first stage [1]. The increase in the activation energy was due to the corrosion reaction mechanism in which charge transfer was blocked by the adsorption of inhibitor molecules on the mild steel surface. It also revealed that the whole process was controlled by the surface reaction since the energy of the activation corrosion process in both the absence and presence of inhibitors was greater than 20 kJ mol^{-1}. In Table 2, the values of ΔH_a and E_a are nearly the same and are higher in the presence of purpald than in a blank solution, indicating that the energy barrier of the corrosion reaction increased in the presence of the inhibitor without changing the mechanism of dissolution.

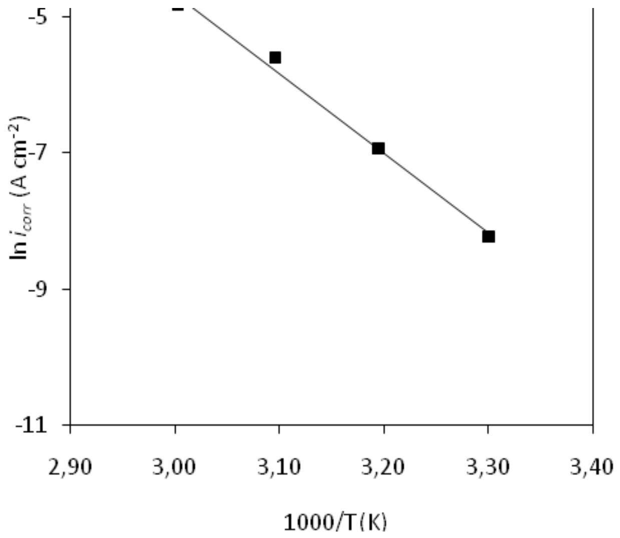

Figure 5. Arrhenius plots for mild steel in 2.5 M H_2SO_4 in the absence and presence of 0.4mM concentration of purpald.

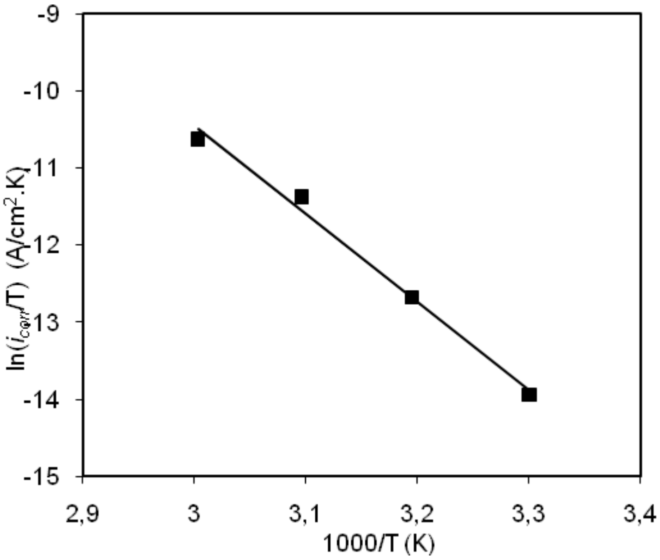

Figure 6. Transition state plots for mild steel in 2.5 M H_2SO_4 in the absence and presence of 0.4mM concentration of purpald.

The entropy of activation, ΔS_a, was negative both in the absence and presence of the purpald implying that the activated complex represented the rate-determining step with respect to the association rather than the dissociation step. This implies that a decrease in disorder occurred when proceeding from the reactants to the activated complex. In addition, the less negative value of ΔS_a in the presence of purpald implies that the presence of inhibitor created a near-equilibrium corrosion system state .

3.4. Adsorption isotherm

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbed on the mild steel surface must be known. The degree of surface coverage (θ) for the inhibitor was obtained from the polarization measurements [10] and is depicted in Tables 1. It was assumed that the adsorption of purpald would follow the Langmuir adsorption isotherm. The plot of C_{inh}/θ versus C_{inh} (Figure 7) yields a straight line, supporting the assumption that the adsorption of purpald from sulfuric acid solution on the mild steel surface at the studied temperature obeys a Langmuir adsorption isotherm, which is represented by eq. 6 [11]

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (6)$$

From the intercepts of the straight lines on the C_{inh}/θ axis, one can calculate K_{ads} values that relate the standard free energy of adsorption, ΔG^0_{ads}, as given by equation (2.23) and by introducing the concentration of water molecules will yield eq. 7:

$$\Delta G^{0}_{ads} = -RT\ln(55.5K_{ads}) \qquad (7)$$

The value, 55.5, in the above equation is the concentration of water in solution in M. Free energies (ΔG^{0}_{ads}) was calculated to be -37.05 kJ/mole; the negative values of ΔG^{0}_{ads} indicate spontaneous adsorption of the inhibitors on the mild steel surface as well as a strong interaction between the inhibitor molecules and the metal surface [10]. Generally, values of ΔG^{0}_{ads} up to -20 kJ/mol are consistent with physisorption, while those around -40 kJ/mol or higher are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate [8]. The calculated ΔG^{0}_{ads} values for purpald was between -40 kJ mol^{-1} and -20 kJ mol^{-1} ,indicating that the adsorption mechanism of the purpald on mild steel in a 2.5 M sulfuric acid solution at 30 °C was a combination of both physisorption and chemisorptions.

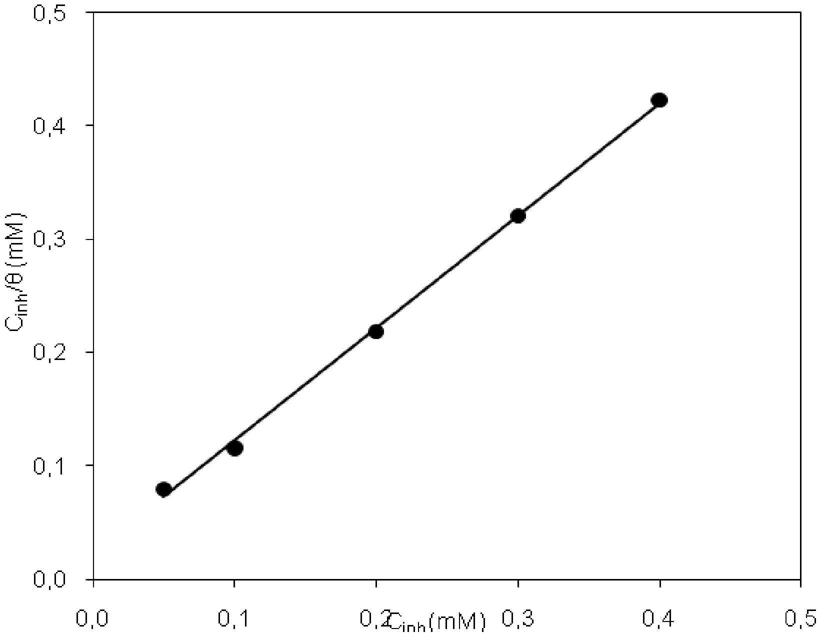

Figure 7. Adsorption isotherms of the purpald on the mild steel surface in a 2.5 M H_2SO_4 solution at different temperatures

4. CONCLUSION

- Purpald compounds can adsorb on the mild steel surface and block the active sites decreasing the corrosion rate.
- Polarization curves indicated that the purpald behaves mainly as mixed-type inhibitor.
- Inhibition efficiencies increase with increasing inhibitor concentration.
- Adsorption mechanism of the purpald on mild steel in a 2.5 M sulfuric acid solution at 30 °C was a combination of both physisorption and chemisorptions.

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