

Corrosion Inhibition Propargyl Alcohol on Low Alloy Cr Steel in 0.5 M H₂SO₄ in the Absence and Presence of Potassium Iodide

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ABSTRACT

The corrosion and inhibition behaviors of low alloy Cr steel in sulfuric acid in the presence of propargyl alcohol (PA) and potassium iodide (KI) have been studied using Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization method. It was found that the inhibition efficiency increased with PA concentration. The addition of potassium iodide to propargyl alcohol in solution increased the inhibition efficiency of propargyl alcohol. A synergistic effect was observed between KI and PA with optimum of concentration of 10 mMol propargyl alcohol + 0.01% potassium iodide. Adsorption of propargyl alcohol alone or in combination with potassium iodide on the metal surface obeyed the Langmuir adsorption isotherm and thermodynamic calculations revealed that the adsorption of inhibitors were of physical nature. That suggest the presence of iodide ions in solution increases the surface coverage.

Key Words: *Inhibitor, Propargyl alcohol, Potassium iodide, Synergistic.*

1. INTRODUCTION

Corrosion problems in the oil and petrochemical industry usually have been solved by the selection of suitable materials and/or by changing the environment to make it less aggressive. Acid solutions are widely used in the industry. The most important areas of application are acid pickling, industrial acid cleaning, acid descaling and oil-

well acidizing [1]. Corrosion inhibitors are needed to reduce the corrosion rates of metallic materials in these acid media. Acetylenic alcohols are considered to be an excellent class of inhibitors to reduce corrosion rates and hydrogen embrittlement of steels in acidic environments. Propargyl Alcohol (PA) (2-propyn-1-ol) is one of the

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acetylenic alcohols and the inhibition effect of PA has been discussed extensively [2-8]. The decisive role of the triple bonds of the PA molecule due to the p-electrons interacting with the metallic surfaces is generally accepted. However, two possible mechanisms were mainly proposed to explain the inhibition effect of PA or its derivatives on iron or steel in both sulfuric and hydrochloric acids [9]:

1. The formation of protective film by polymerization of PA on active metallic surface[1,10].
2. The adsorption of PA on metal surfaces and its chemical conversion influences the kinetics and mechanism of the anodic and/or cathodic reactions[9].

In impedance corrosion studies of iron in H₂SO₄ in presence of PA, Epelboin et al, introduced the charge transfer resistance R_t as a parameter more closely related to corrosion rate than the polarization resistance[10]. The inhibiting effect of PA in hydrochloric acid solutions is much higher than that in sulfuric acid solutions. Some studies suggest that the chloride ions have a stronger tendency to adsorb than do sulfate ions and the electrostatic influence on the inhibitor adsorption may be the reason for an increased protective effect in halide-containing solution[11,12]. However, comparatively fewer experimental data are available for the synergistic effect between iodide ions and propargyl alcohol [9]. Padobave et al. investigated the effect anions and inhibition mixed with propargyl alcohol on electrode reaction and corrosion steel in sulfuric acid[13].

The present work aims to investigate, the synergistic behavior between PA and iodide ions in 0.5 M sulfuric acid solutions, using electrochemical methods.

2. EXPERIMENTAL

In this study, the samples for the electrochemical measurements were taken of low alloy Cr steel with an exposed area of 1 cm² and following composition (Fe:95.80% ; C:0.51% ; Mn:1.19% ; Cr:2.06% ; S:0.38%). Before each run of experiments, they were mechanically polished successively with different grades of emery papers (from grade #300 to #1200), washed with double distilled water, degreased with ethanol and dried, then placed in a test solution for 30 min of immersion before electrochemical measurements. Each test duplicated.

In these experiment, a platinum and a Saturated Calomel Electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The working electrode (WE) was a low alloy Cr steel specimen. All potentials were measured against SCE (0.244 vs. SHE).

Electrochemical impedance spectroscopy (EIS) and potentiodynamic scanning (PDS) were conducted in an electrochemical measurement system which comprises a EG&G potentiostat/galvanostat model 263A, a personal computer and powersuit software.

The AC impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 100

kHz–10 Hz, with a signal amplitude perturbation of ±10 mV. The linear polarization (LP) measurements were carried out, after the impedance test a potentiodynamic scan (PDS) was performed over a potential range from -0.25 to +0.25 V vs. open circuit potential (E_{ocp}) at a scan rate of 1 mV/s. Values of the corrosion current density (I_{corr}) were determined by extrapolation of the cathodic and anodic Tafel lines to the corresponding corrosion potentials.

A 0.5M H₂SO₄ solution was prepared from sulfuric acid (98%) and double distilled water which was used as a corrosion media in this study. Propargyl Alcohol (PA) (HC≡C-CH₂-OH) was dissolved in 0.5 M H₂SO₄ solution to obtain different desired PA concentrations. 0.01% potassium iodide (KI), was also used in this study. All experiments were carried out at room temperature (Each test duplicated).

3. RESULTS AND DISCUSSION

3.1. Impedance Measurements

Figure 1 shows Nyquist plots for low alloy Cr steel in 0.5M H₂SO₄ solution in the absence of inhibitor (curve B) and in the presence of 1.25 mMol propargyl alcohol (curve 1.25mM PA). For curve B, a big semicircle was observed in the highest frequency region and a very small indications of inductive loops in the lowest frequency region that related to adsorption of ions such as (SO₄²⁻)_{ads} and (H⁺)_{ads}. The addition of propargyl alcohol to the solution caused a big semicircle in the highest and lowest frequency region and illustrates that the corrosion process is controlled by charge transfer resistance. The impedance spectra were modeled with equivalent circuits shown in Figure 2. The dissimilar equivalent circuit models for these Nyquist plots in Figure 2, clearly illustrate difference in mechanism for dissolving low alloy Cr steel in 0.5M H₂SO₄ solution in the absence of inhibitor and in the presence of PA. The equivalent circuit shown in Figure 2.b. In this circuit, C_{dl} is the double layer capacitance, R_t is the interfacial charge-transfer resistance, L is the inductance, and R_L is the inductive resistance (dissolving low alloy Cr steel in 0.5M H₂SO₄ solution in the absence of PA)

The equivalent circuit shown in Figure 2.b (dissolving low alloy Cr steel in 0.5M H₂SO₄ solution in the presence of PA) contains constant phase element (CPE) instead of ideal capacitor. The impedance of CPE has the form [14]:

$$Z_{CPE} = (1/Y_0) [(j\omega)^n]^{-1} \quad (1)$$

Where Y₀ is the magnitude of CPE, j is the imaginary number (j²=-1) and n can be used as a gauge of the heterogeneity of the surface. Both Y₀ and n are independent from frequency and $n = \alpha/(\pi/2)$. The α is the phase angle of CPE and decrease of α equal to increase of the heterogeneity of the surface. Depending on n, CPE can represent resistance (n = 0, CPE = R), capacitance (n = 1, CPE = C), inductance (n = -1, CPE = L) or Warburg impedance (n = 0.5, CPE = W). The value of n is often between 0.5 and 1 [15, 16].

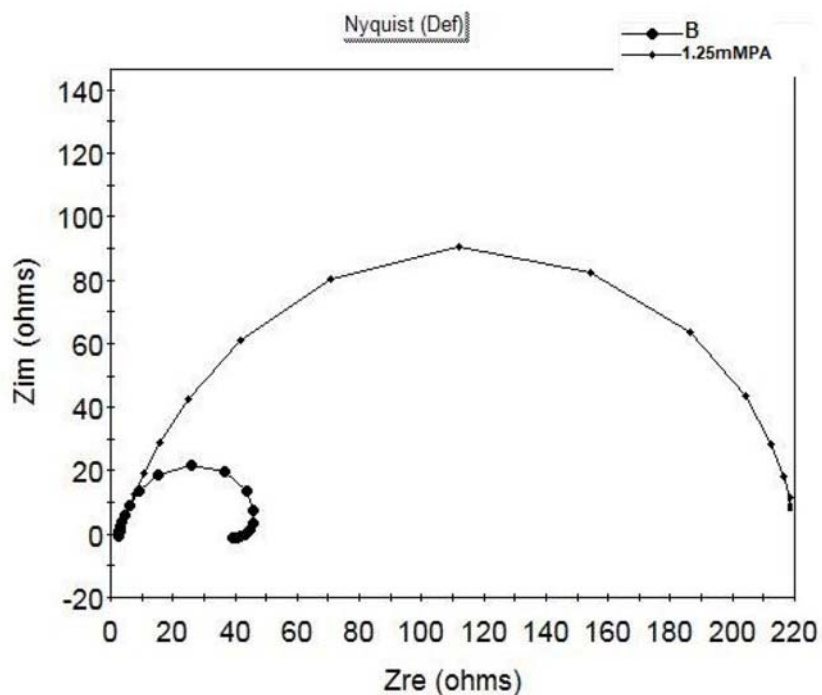


Figure 1. Nyquist plots for low alloy Cr steel in 0.5 M H₂SO₄ solution in the absence of inhibitor (curve B) and in the presence of 1.25 mM propargyl alcohol (curve 1.25mM PA).

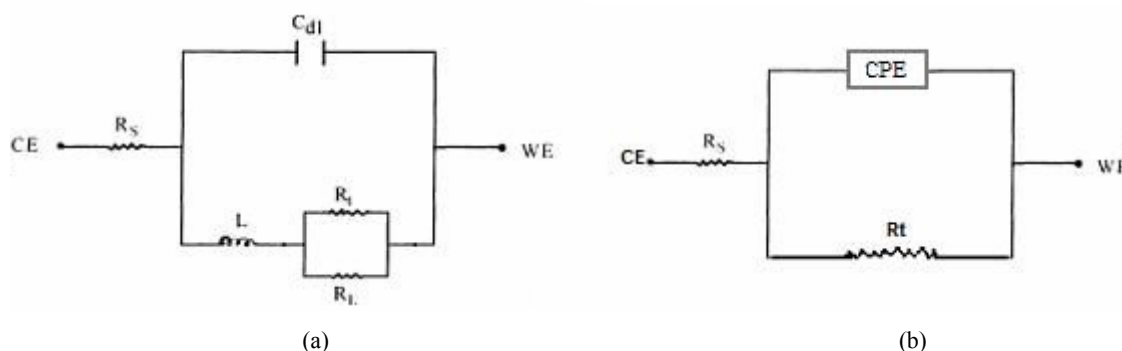


Figure 2. The equivalent circuit models for dissolving low alloy Cr steel in 0.5 M H₂SO₄ solution in the absence of inhibitor (a) and in the presence of PA (b).

Figure 3 shows Nyquist plots for low alloy Cr steel in 0.5M H₂SO₄ solution in the presence of different concentrations of PA. Increase of PA concentration lead to increase of diameter of semicircles, and accompanied by increase of charge transfer resistance. Also in Figure 4

that shows Nyquist plots for low alloy Cr steel in 0.5 M H₂SO₄ solution in the presence of different concentrations of PA and 0.01% KI, increase of charge transfer resistance was greater.

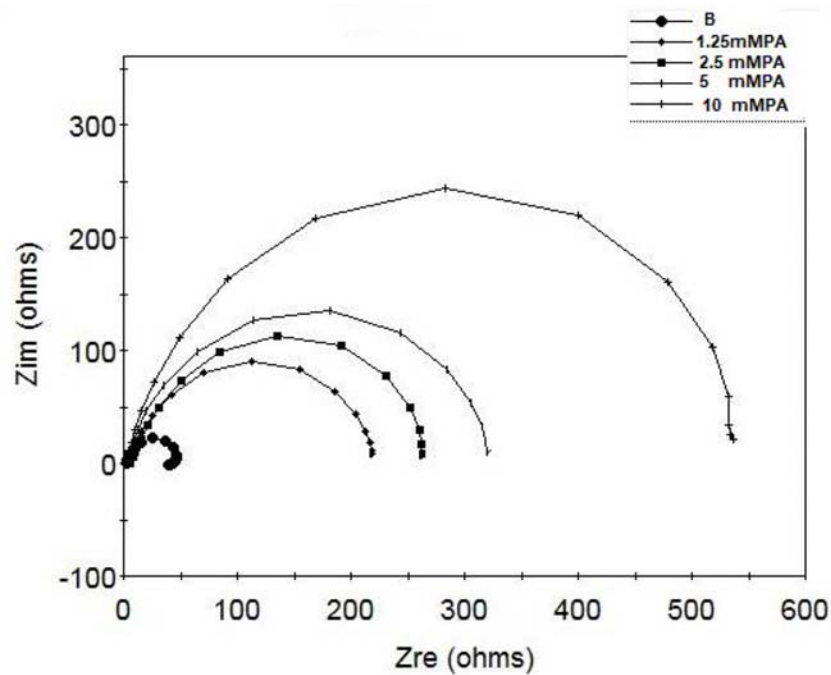


Figure 3. Nyquist plots for low alloy Cr steel in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of PA.

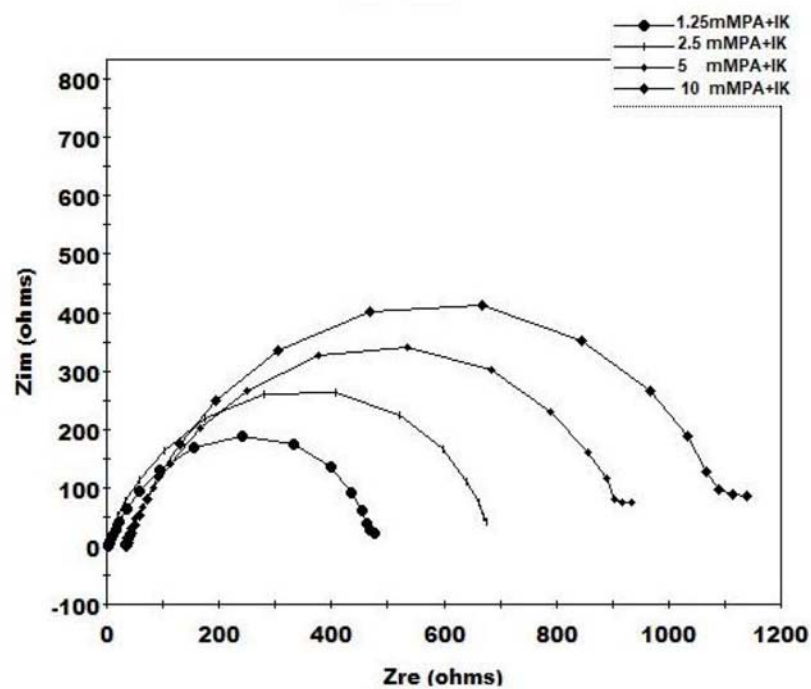


Figure 4. Nyquist plots for low alloy Cr steel in 0.5 M H₂SO₄ solution in the presence of different concentrations of PA and 0.01% KI.

The value of charge transfer resistance (R_t) is obtained from the difference between real impedance in the highest and lowest frequency region and then according to below equation (2) and (3) the values of inhibition efficiency $\eta(\%)$ and the double layer capacity (C_{dl}) can be calculated, respectively [17,18].

$$\eta(\%) = \frac{R_{t_i} - R_{t_0}}{R_{t_i}} \times 100 \quad (2)$$

Where R_{t_0} and R_{t_i} are the charge transfer resistance values without and with inhibitor, respectively.

$$C_{dl} = \frac{1}{2\pi W_{max} R_t} \quad (3)$$

Where C_{dl} is the double layer capacity; R_o the charge transfer resistance value; and W_{max} the frequency at which the impedance imaginary is maximum.

Table 1 gives the double layer capacity, the charge transfer resistance values and inhibition efficiency values for different concentrations of PA in the absence and

presence of 0.01% KI in 0.5M H_2SO_4 solution. The increase of PA concentration lead to increasing inhibition efficiency, increasing the charge transfer resistance values and decreasing the double layer capacity due to forming a more compact adsorption layer on the surface. The addition of 0.01% KI to the solution caused the influence of PA increase.

Table 1. The results obtained from Nyquist plots for low alloy Cr steel in 0.5 M H_2SO_4 solution in the presence of different concentrations of PA and of 0.01% KI.

PA Conc (mM)	KI Conc (W%)	$R_t(\Omega cm^2)$	$C_{dl}(\mu F/cm^2)$	$\eta(\%)$
Blank	-	35.6	919.7	-
1.25	-	214.3	678.6	83.3
1.25	0.01	474.5	556.6	92.3
2.5	-	252.8	542.3	85.9
2.5	0.01	675.2	405.8	94.7
5	-	322.2	454.8	88.9
5	0.01	906.9	313.9	96.1
10	-	532.3	255.5	93.3
10	0.01	1108.5	245.5	96.7

3.2. Polarization Curves

Figure 5. shows the Tafel polarization curves of low alloy Cr steel in 0.5 M H_2SO_4 blank solutions (curve Blank) and in the presence of different concentrations (1.25–10 mM) of PA. With the increase of PA concentration, the

curves were shifted to left and both anodic and cathodic currents were reduced, however the anodic polarization curves were shifted to right at anodic voltage ≥ -350 mV in the presence of PA. This indicate that PA molecules are desorbed from the low alloy Cr steel surface at these anodic potentials.

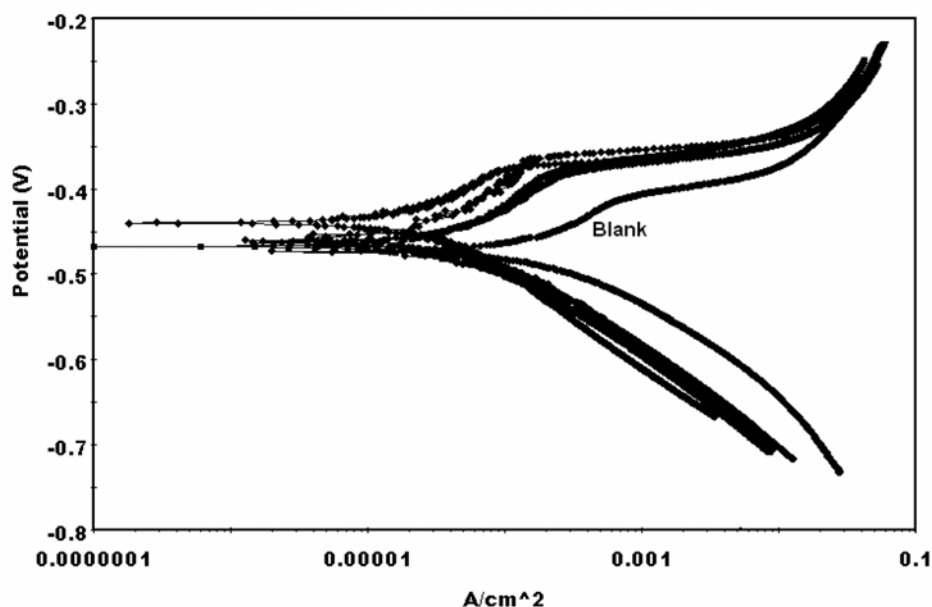


Figure 5. The Tafel polarization curves of low alloy Cr steel in 0.5 M H_2SO_4 blank solutions (curve Blank) and in the presence of different concentrations (1.25–10 mM) of PA.

Figure 6. shows the polarization curves of low alloy Cr steel in 0.5 M H₂SO₄ blank solutions (curve Blank) and in the presence of different concentrations (1.25–10 mM) of PA and 0.01% KI. The addition of KI to the solution caused more decrease in corrosion current density in the presence different of concentrations of PA. The anodic

polarization curve was shifted to right at anodic voltage ≥ -350 mV in the presence of 1.25mM PA and 0.01% KI, but this didn't occur in the presence of other concentrations of PA. Hence, the desorption of adsorbed inhibitor from the low alloy Cr steel surface in these concentrations of PA are less occurred [19].

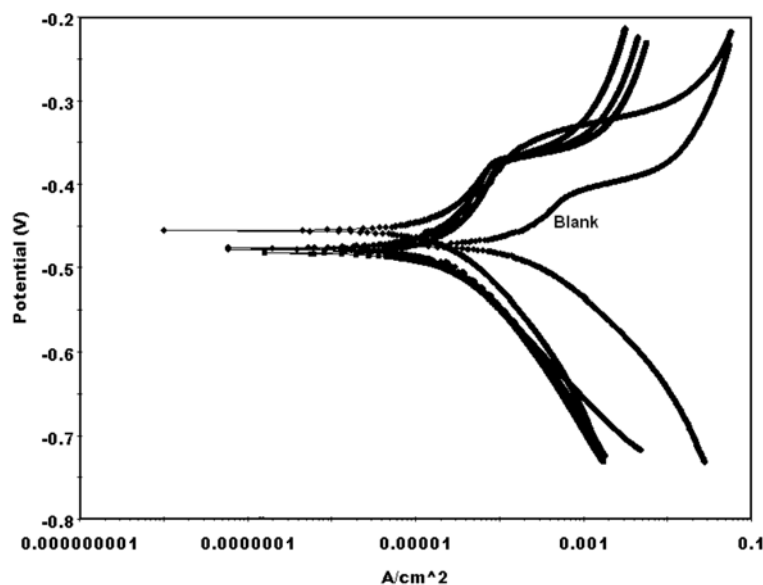


Figure 6. The Tafel polarization curves of low alloy Cr steel in 0.5 M H₂SO₄ blank solutions (curve Blank) and in the presence of different concentrations (1.25–10 mM) of PA and 0.01% KI.

Table 2 gives the corrosion current density and the inhibition efficiency values for different concentrations of PA in the absence and presence of 0.01% KI in 0.5 M H₂SO₄ solution which were obtained from the polarization curves. Values of the corrosion current density (I_{corr}) were determined by extrapolation of anodic and cathodic Tafel lines 50mV up and down of corrosion potential (E_{corr}). The inhibition efficiency values were obtained from bellow equation [18].

$$\eta(\%) = \frac{I_0 - I_i}{I_0} \times 100 \quad (4)$$

Where I_0 and I_i are the corrosion current densities in the absence and the presence of the inhibitor, respectively.

With the increase of PA concentration, the corrosion potential approximately were unchanged, but the corrosion current density decreased and the inhibition efficiency increased. Addition 0.01% KI to the solution caused more increase in the inhibition efficiency, however the corrosion potential approximately were unchanged. It can be concluded that propargyl alcohol in the absent and the present of the potassium iodide inhibit corrosion process by affecting the cathodic and anodic surfaces, hence, PA and KI are mixed anodic-cathodic type inhibitors.

Table 2. The results obtained from the Tafel polarization curves for low alloy Cr steel in 0.5M H₂SO₄ solution in the presence of different concentrations of PA and of 0.01% KI.

PA Conc (mM)	KI Conc (W%)	E_{corr} (mV)	I_{corr} (μ A/cm ²)	$\eta(\%)$
Blank	-	-476	278	-
1.25	-	-463	108	61.1
1.25	0.01	-476	30	89.2
2.5	-	-468	80	71.2
2.5	0.01	-482	27	90.2
5	-	-460	40	85.6
5	0.01	-478	22	92.1
10	-	-440	31	88.8
10	0.01	-455	17	93.9

3.3. Synergism Parameter

To evaluate the synergistic effects between the two inhibitors, synergism parameter (S) can be established as follows:

$$S = \frac{I_1 I_2}{I_{1,2} I_0} \tag{5}$$

Where I_0 is corrosion current density for the blank solution; I_1 and I_2 are corrosion current densities in the presence of PA and KI, respectively; and $I_{1,2}$ corrosion current density in the presence of PA and KI, simultaneously. S approaches 1 when no interaction between the two inhibitors exists, while $S > 1$ points to a synergistic effect. In the case of $S < 1$, the antagonistic interaction predominates [18]. The corrosion current density in the presence of 0.01% KI was obtained from polarization curves ($I_{KI} = 158 \mu A/cm^2$). Table 3 gives values of the synergism parameter (S) which is calculated for different concentrations of PA and 0.01% KI, by using polarization curves data. Values of S for the PA and KI are greater than unity. This result indicates that the increase in inhibitor efficiency is generated by the addition of KI to PA due to a synergistic effect and this may be related to adsorption of iodide ions on metal surfaces that caused the increase of adsorption of inhibitors.

Table 3. Values of the synergism parameter (S) for different concentrations of PA and 0.01% KI.

PA (mM)	S
1.25	1.26
2.5	1.24
5	1.14
10	1.12

3.4. Adsorption Isotherm

Adsorption isotherms are often shown to demonstrate the performance of organic adsorbent type inhibitors. The simplest, being Langmuir isotherms, is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not. Langmuir isotherm can be expressed as [20]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{6}$$

Where C_{inh} is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant. In this case θ is numerically identical to the percentage inhibition efficiency, obtained from polarization or impedance techniques, and divided by 100 ($\theta = \eta / 100$). Regarding to the equation (6), a linear relationship observed when C_{inh} / θ is plotted as a function of C_{inh} , with a slope of ideally unity. In the following, the impedance data, reported in Table 1, were used for calculations.

A plot C_{inh} / θ versus C_{inh} give a straight lines as seen from Fig 7-8 therefore the adsorption of PA alone and in combination with KI from sulfuric acid 0.5 M on the low alloy Cr steel surface obey the Langmuir isotherm.

The value of K_{ads} is found as $38.74 \times 10^3 \text{ dm}^3/\text{Mol}$ and $144.92 \times 10^3 \text{ dm}^3/\text{Mol}$ For PA and PA+0.01% KI respectively. The increasing value of K_{ads} of PA+0.01% KI to PA alone reflects the increasing adsorption capability [5]. The free energy of adsorption was calculated according to the following equation.

$$\Delta G_{ads} = -RT \ln K_{ads} \tag{7}$$

Where R is the universal gas constant and T is the absolute temperature [21]. These values of ΔG_{ads} were found to $-23.74 \text{ KJ mol}^{-1}$ and $-20.46 \times 10^3 \text{ KJ mol}^{-1}$ for PA+0.01%KI and PA. The increasing value of ΔG_{ads} (toward the negative) reflects the increasing adsorption capability and the negative value of ΔG_{ads} indicates spontaneous adsorption of inhibitor molecule on the metal surface [22].

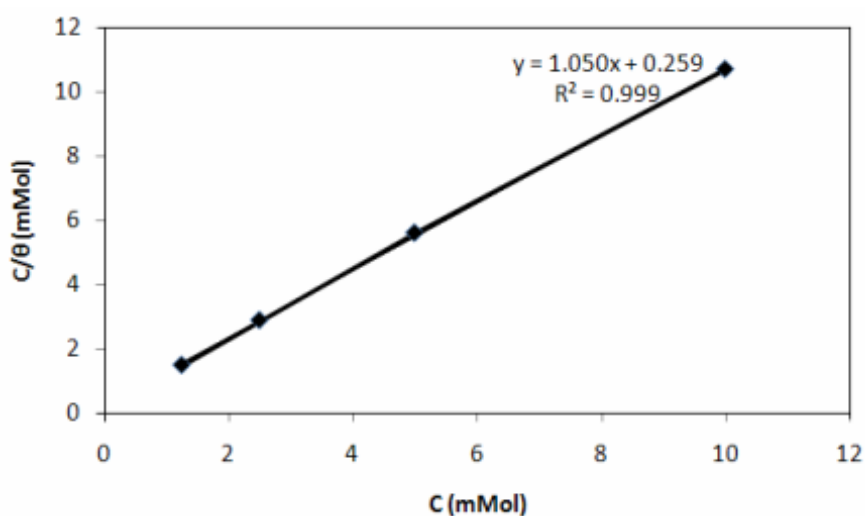


Figure 7. Langmuir adsorption plots for low alloy Cr steel in 0.5M H₂SO₄ containing PA.

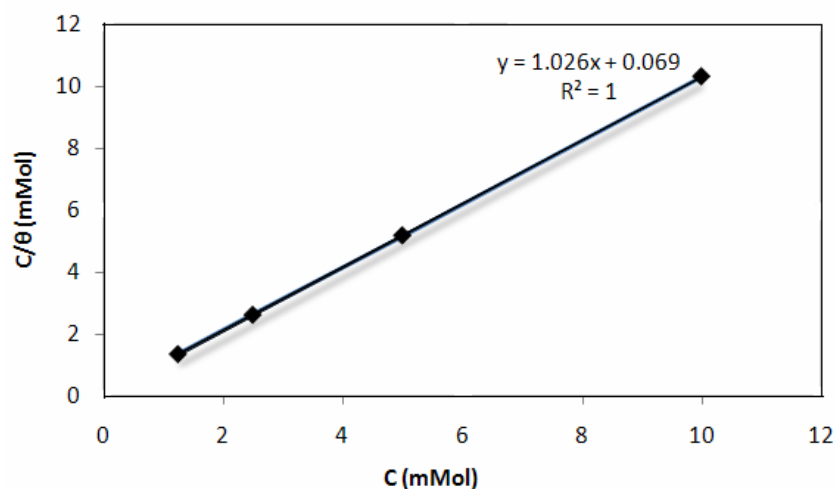


Figure 8. Langmuir adsorption plots for low alloy Cr steel in 0.5M H₂SO₄ containing PA + 0.01% KI.

4. CONCLUSION

1-The data obtained from the Tafel polarization curves and electrochemical impedance spectroscopy (EIS), approve that propargyl alcohol and potassium iodide are effective corrosion inhibitors for low alloy Cr steel in 0.5 M sulfuric acid solution.

2-The inhibition efficiency improved with the increase of PA concentration, whether PA was used alone or in combination with KI. The increase in inhibitor efficiency is generated by the addition of KI to PA.

3-The Tafel polarization curves indicate that both propargyl alcohol and potassium iodide are mixed anodic-cathodic type inhibitors.

4-The addition 0.01% KI to the solution lead to reduction in the essential usage of PA to achieve a desirable inhibition efficiency. Because propargyl alcohol is more expensive than potassium iodide, this could decrease the inhibition costs drastically.

5-The adsorption of PA alone and in combination with KI from sulfuric acid 0.5 M on the low alloy Cr steel surface obey the Langmuir isotherm.

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