Inhibition impact of 1-phenyl-2-pyrazolin-5-one derivatives on corrosion of 304 stainless steel in molar HCl solution

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Abstract

Chemical and electrochemical methods such as weight loss (WL) method, potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM) techniques were utilized to study 1-phenyl-2-pyrazolin-5-one (PPO) derivatives as safe corrosion inhibitors for 304 stainless steel (SS 304) in 1.0 M HCl. The inhibition efficiencies and adsorption characteristics were determined from the WL results. The results indicated that the protection efficiency (%IE) rises with an increase in the concentration of 1-phenyl-2-pyrazolin-5-one derivatives. The adsorption of these derivatives on the surface of SS 304 follows the Langmuir isotherm. The 1-phenyl-2-pyrazolin-5-one derivatives are good inhibitors for the dissolution of SS 304 in 1 M HCl and they are mixed-type inhibitors. Analysis of data on the free adsorption energy of 1-phenyl-2-pyrazolin-5-one derivatives on the surface of SS 304 in acid media frequently allows assuming the chemisorption character of their interaction, which to a large extent explains the efficiency of these compounds in corrosion inhibition. At 298 K, atomic force microscopy (AFM) was used to examine the coupon surface morphology without and with inhibitors at a concentration of $24 \cdot 10^{-6}$ M. The development of a protective layer of derivative molecules on the coupon surface in the hydrochloric acid solution at 298 K is suggested by AFM. Density functional theory (DFT) quantum chemical computations were used to determine the relationship between the electronic structural characteristics of the 1-phenyl-2-pyrazolin-5-one derivative molecules and the inhibitory efficiency. HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), E (energy gap), μ (dipole moment), and A_0 (molecular surface area) were computed. The quantum chemical parameters of the studied inhibitors estimated using the DFT technique accord with the experimental inhibitory efficiency.

Received: August 15, 2021. Published: October 8, 2021

doi: [10.17675/2305-6894-2021-10-4-3](https://doi.org/10.17675/2305-6894-2021-10-4-3)

Keywords: corrosion inhibition, 304 stainless steel, EIS, EFM, SEM, AFM, DFT.

Introduction

Stainless steel has high mechanical properties and good corrosion resistance, so it is considered a popular choice among construction materials widely utilized in the majority of manufacturing areas [1, 2]. The corrosion resistance of these metal alloys has been attributed to an oxide film formed on the surface of SS [3, 4]. Nowadays, the dissolution resistance of 304 SS often has to be improved using corrosion protectors. Specifically, the corrosion hindrance of 304 SS in an acid environment with inhibitors is very important as the alloy is often exposed to acids throughout various procedures. The impact of numerous organic inhibitors in corrosion hindrance of 304 SS in the acid environment has been examined [5, 6]. Organic compounds comprising an N, O, S, or P atom (*i.e.*, hetero-atoms), multiple bonds or aromatic systems which can be adsorbed on the surface of an alloy *via* a lone pair of electrons and/or π -electrons are frequently confirmed to be remarkably effective inhibitors of dissolution [7, 8]. Several 2-pyrazolin-5-one derivatives are known to display diverse pharmacological activities such as analgesics, antipyretics and anticancer agents [9–11]. In this study, the impact of PPO compounds as safe inhibitors for dissolution of 304 SS in 1 M HCl was tested. The PPO compounds were chosen as corrosion inhibitors because PPO compounds contain multiple active centers and have a distinct affinity to protect SS 304 corrosion in HCl. Finally, several methods, including theoretical and experimental ones, have been used to study the inhibition behavior of PPO compounds against SS 304 corrosion in 1 M HCl.

Materials and Methods

Materials and solutions

The SS 304 specimens used for WL and electrochemical tests have the following chemical composition (wt.%): 0.08 C, 0.75 Si, 18–20 Cr, 2.0 Mn, 10.5 Ni, 0.045 P and the rest Fe.

The examined PPO compounds were synthesized according to the procedures demonstrated in previously published papers [9–11]. These compounds are shown in Table 1. The corrosive solution was prepared by diluting analytical reagent grade 34% HCl with distilled water to obtain the desired concentration of 1 M HCl. The 10^{-3} M stock solutions of 2-chlorophenyl hydrazine (PPO) derivatives were dissolved in the smallest amount of dimethyl formamide (DMF) and completed with ethanol and then diluted with distilled water to the final concentrations ranging from $4 \cdot 10^{-6}$ – $24 \cdot 10^{-6}$ M).

Table 1. The chemical structure of PPO derivatives.

Inhibitor	Structure
PPO-1	<p>(<i>E</i>)-4-(2-(4-chlorophenyl)hydrazineylidene)-2-phenyl-5-(phenylamino)-2,4-dihydro-3<i>H</i>-pyrazol-3-one Molecular Weight: 389.84</p>
PPO-2	<p>(<i>E</i>)-5-amino-4-(2-(4-chlorophenyl)hydrazineylidene)-2-phenyl-2,4-dihydro-3<i>H</i>-pyrazol-3-one Molecular Weight: 313.75</p>
PPO-3	<p>(<i>E</i>)-4-(2-(4-chlorophenyl)hydrazineylidene)-1-phenylpyrazolidine-3,5-dione Molecular Weight: 314.73</p>

Corrosion inhibition evaluation

WL test

Samples of 304 stainless with a dimension of $2 \times 2 \times 0.2 \text{ cm}^3$ were scratched with various grades of emery papers from 400 to 1200, rinsed with doubled-distilled water many times, and dried. They were weighed exactly and immersed for 3 h in a glass bottle (open system) containing 50 ml of HCl in the presence and in the absence of various concentrations of PPO

compounds. After every 30 min, 304 SS samples were withdrawn, washed, dried, and weighed thoroughly. The average WL ($\text{mg}\cdot\text{cm}^{-2}$) of seven SS 304 coins should be obtained. The degree of surface coverage (θ) and (%IE) of PPO for SS 304 dissolution in 1 M HCl were measured from Equations 1 and 2, respectively:

$$\theta = \left[1 - \frac{W}{W^0} \right] \quad (1)$$

$$\%IE = \left[1 - \frac{W}{W^0} \right] \cdot 100 \quad (2)$$

where W^0 and W are the values of the average WL without and with addition of PPO compounds, respectively.

Electrochemical tests

All electrochemical measurements were performed in a three-electrode electrochemical cell including an SS 304 working electrode, an Ag/AgCl reference electrode, and a platinum disk as the counter electrode. Before each electrochemical test, the SS 304 electrode was dipped for 30 min in the solution to allow the open circuit potential (OCP) to achieve a steady state. Each experiment was achieved on a freshly abraded electrode utilizing a newly prepared electrolyte.

PP was performed by sweeping the electrode potential from -500 to 500 mV vs. (OCP) at a sweep rate of $1 \text{ mV}\cdot\text{s}^{-1}$. (%IE) and (θ) were determined from (i_{corr}) in Equation (3).

$$\%IE = \theta \cdot 100 = \left[1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right] \cdot 100 \quad (3)$$

where i_{corr}^0 and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

EIS tests were carried out by applying AC signals in the range from 100 kHz to 0.1 mHz with a peak amplitude of 5 mV at OCP. All the impedance data were consistent with the suitable equivalent circuit employing the Gamry Echem program, and (%IE) and (θ) were measured by utilizing the charge transfer resistance (R_{ct}) as a function of the performance of protection.

$$\%IE = \theta \cdot 100 = \left[1 - \frac{R_{\text{ct}}^0}{R_{\text{ct}}} \right] \cdot 100 \quad (4)$$

where R_{ct}^0 and R_{ct} are the charge-transfer resistance values without and with an inhibitor, respectively.

The EFM technique was utilized by relating two sine waves of 2 and 5 Hz [12, 13]. The parameters (i_{corr}), CF-2 and CF-3, and (β_{c} and β_{a}) were measured [14]. (θ) and (%IE) were determined from equation (2) like the PP.

All electrochemical techniques were executed using a Gamry Potentiostat/Galvanostat with PCI4-G750 software for measurements, linked to a PC for data retrieval and storage.

Surface analysis

SS 304 coins were dipped in 1 M HCl in the presence and in the absence for $24 \cdot 10^{-6}$ M PPO compounds for 24 h. The surface morphology of SS 304 stainless coins was studied by Pico SPM2100 for AFM analysis.

Quantum chemical calculations (QM)

QM calculations were performed employing Materials Studio style 7.0 from Accelrys Inc. USA [15–17]. The DMol³ model was utilized for QM by relating GGA technique with DNP basis set and BOP functional enclosing COSMO controls [18–21].

Results and Discussion

WL tests

The WL plots for SS 304 in mg cm^{-2} of the surface area dissolution in 1 M HCl in the presence and in the absence of various concentrations of PPO1 are displayed in Figure 1. The WL–time lines obtained in the presence of PPO1 are found below that of 1 M HCl (blank). When the PPO1 concentration rises, WL decreases, θ rises, and the %IE improves. The %IE values are presented in Table 2. This effect results from the adsorption of PPO on SS 304 surface producing a coating layer that separates the SS 304 from the aggressive environment and reduces the 304 stainless steel dissolution. Consequently, the rate of dissolution decreases with an increase in the concentration [22]. The order of %IE for PPO compounds determined from the calculated values of %IE is as follows: PPO-1 > PPO-2 > PPO-3.

Figure 1. Time–WL diagrams for SS 304 in 1 M HCl with and without various PPO1 concentrations at 30°C.

Table 2. The corrosion rate (C.R.) and (%IE) for SS304 immersed in 1 M HCl without and in the presence of PPO derivatives as determined from WL tests at 30°C.

Inhibitor	Conc., μM	C.R., $\text{mg}\cdot\text{cm}^{-2}\text{min}^{-1}$	θ	%IE
1 M HCl	0	0.0123	–	–
PPO-1	4	0.0027	0.776	77.6
	8	0.0020	0.831	83.1
	12	0.0016	0.867	86.7
	16	0.0015	0.879	87.9
	20	0.0014	0.882	88.2
	24	0.0010	0.916	91.6
PPO-2	4	0.0060	0.514	51.4
	8	0.0054	0.561	56.1
	12	0.0051	0.583	58.3
	16	0.0047	0.617	61.7
	20	0.0042	0.654	65.4
	24	0.0035	0.710	71.0
PPO-3	4	0.0062	0.495	49.5
	8	0.0056	0.542	54.2
	12	0.0049	0.600	60.0
	16	0.0047	0.617	61.7
	20	0.0045	0.636	63.6
	24	0.0041	0.663	66.3

Adsorption isotherm

Several trials were performed to fit the experimental data to various isotherms. Various adsorption isotherms were utilized to fit θ values, including the Frumkin, Langmuir, Temkin, and Freundlich isotherms. It was found that the Langmuir isotherm is the most appropriate isotherm for the data obtained. It can be described by Equation 5 [23]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (5)$$

Where C is the concentration (M) of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage, and K_{ads} is the adsorption equilibrium constant (M^{-1}). The linear regressions of C/θ versus C for PPO are displayed in Figure 2. The K_{ads} values were

determined from the intercepts, and the standard free adsorption energies (ΔG_{ads}^0) were computed from the K_{ads} values as follows [24]:

$$\log K_{\text{ads}} = -\log 55.5 - \frac{\Delta G_{\text{ads}}^0}{2.303RT} \quad (6)$$

where 55.5 is the molar concentration of water in the solution in mol/L, R is the gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature (K).

Figure 2. Langmuir plots for the adsorption of PPO-1 on SS 304 in 1 M HCl at various temperatures.

Figure 3. Plots of $\log K_{\text{ads}}$ vs. $1/T$ for corrosion of SS 304 in 1 M HCl in the absence and presence of various concentrations of PPO derivatives.

The ΔG_{ads}^0 data at all temperatures are presented in Table 3. The (ΔH_{ads}^0) values were assessed based on the Van't Hoff Equation:

$$\log K_{\text{ads}} = -\frac{\Delta H_{\text{ads}}^0}{2.303RT} + \text{constant} \quad (7)$$

Table 3. The adsorption isotherm results for dissolution of SS 304 in 1 M HCl solution in the presence of PPO derivatives at various temperatures.

Inhibitor	Temp, °C	$K_{\text{ads}} \cdot 10^3 \text{ M}^{-1}$	$-\Delta G_{\text{ads}}^0 \text{ kJ} \cdot \text{mol}^{-1}$	$-\Delta H_{\text{ads}}^0, \text{kJ} \cdot \text{mol}^{-1}$	$\Delta S_{\text{ads}}^0, \text{J mol}^{-1} \text{K}^{-1}$
PPO-1	30	931.2	44.8	13.4	103.6
	35	864.7	45.3		103.7
	40	771.5	45.8		103.5
	45	732.6	46.5		403.7
PPO-2	30	268.3	41.6	26.1	51.2
	35	217.7	41.8		50.9
	40	184.7	42.0		50.9
	45	164.8	42.4		51.3
PPO-3	30	326.5	42.1	66.4	−80.3
	35	260.1	42.2		−78.6
	40	141.2	41.3		−80.2
	45	100.3	41.1		−79.7

Plotting ($\log K_{\text{ads}}$) vs. ($1/T$) gives a straight line as demonstrated in Figure 3; the slope is ($-\Delta H_{\text{ads}}^0/2.303R$). The ΔH_{ads}^0 data obtained from this slope are shown in Table 3. Then by applying the subsequent Equation (8) [25]:

$$\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0 \quad (8)$$

The data presented in Table 3 confirm the spontaneous adsorption of PPO derivatives on SS304 surfaces. The negative ΔG_{ads}^0 value (spontaneous) greater than 40 kJ/mol are indicative of chemical adsorption by creation of coordinate bonds between an active site of PPO (N, O, benzene ring) and empty d-orbitals of iron, or perhaps due to complex formation with Fe^{2+} ions on SS surface [26, 27]. The negative sign of ΔH_{ads}^0 for the PPO indicate that the adsorption of PPO compounds is an exothermic process. ΔS_{ads}^0 had a positive sign for PPO-1 and PPO-2 with no noticeable variation at various temperatures, suggesting that PPO molecules adsorption is accompanied by desorption of water molecules from the SS304 surface, which increases the randomness [28]. Moreover, ΔS_{ads}^0 had a negative sign for PPO-3 with no noticeable variation with temperature, suggesting that more inhibitor molecules are arranged on the metal surface than dispersed in solution [29].

PP evaluation

The PP plots for SS 304 dissolution in 1 M HCl and in the presence and in the absence of various PPO1 concentrations at 25°C are demonstrated in Figure 4. The measured values of E_{corr} , i_{corr} from the Tafel curve (i_{corr}^0), θ and %IE are reported in Table 4 [30]. The parallel Tafel lines, β_a and β_c indicate that both anodic and cathodic mechanisms are not affected by addition of the PPO to the corrosive environment. The data in Table 4 displays that the lower i_{corr} values in the presence of PPO does not affect considerably the E_{corr} , thus suggesting that the PPO is a mixed kind of inhibitor [31, 32]. The behavior of %IE for the PPO compound signifies that it hinders both anodic and cathodic reactions on SS304 in 1 M HCl by protecting the active centers [33]. The order of %IE for the PPO is: PPO-1>PPO-2>PPO-3, which agrees with the results obtained from weight loss measurements.

Figure 4. PP for SS 304 in 1 M HCl without and with various concentrations of PPO-1 at 25°C.

Table 4. Polarization results for SS 304 in 1 M HCl without and with various concentrations of PPO derivatives at 25°C.

Concentration, μM	i_{corr} , μAcm^{-2}	$-E_{\text{corr}}$, mV	b_a , mV/decade	$-b_c$, mV/decade	C.R., mpy	θ	%IE	
1 M HCl	71.10	354.0	46.3	105.7	32.47	—	—	
PPO-1	4	23.60	359.0	43.6	129.0	10.80	0.668	66.8
	8	20.60	346.0	40.3	127.0	9.39	0.710	71.0
	12	14.80	334.0	38.8	123.6	6.76	0.792	79.2
	16	10.40	337.0	41.6	120.7	4.75	0.854	85.4
	18	8.52	328.0	37.0	145.6	3.89	0.880	88.0
	20	6.20	338.0	36.3	139.1	2.59	0.913	91.3
PPO-2	4	28.30	348.0	43.0	132.0	12.91	0.602	60.2
	8	23.40	334.0	40.2	129.6	10.68	0.671	67.1
	12	21.40	351.0	46.9	126.2	9.76	0.699	69.9
	16	19.5	347.0	35.0	124.6	8.90	0.726	72.6
	18	17.10	345.0	35.5	127.1	7.82	0.759	75.9
	20	12.80	348.0	44.3	113.5	5.82	0.820	82.0
PPO-3	4	35.60	354.0	53.9	128.6	16.27	0.499	49.9
	8	31.40	352.0	42.4	131.8	14.32	0.558	55.8
	12	27.40	348.0	47.1	130.5	15.52	0.615	61.5
	16	25.50	346.0	40.3	128.3	11.65	0.641	64.1
	18	22.90	347.0	43.9	135.5	10.47	0.678	67.8
	20	18.20	340.0	46.7	124.7	8.33	0.744	74.4

Electrochemical impedance measurements

Figures 5a, b display the Nyquist and Bode plots for SS 304 surface immersed in 1.0 M HCl in the absence and in the presence of various PPO-1 concentrations at 25°C. As the PPO-1 concentration decreases, the diameter of the semicircle increases [34]. The deviation from the perfect semicircle is normally due to the dispersal of frequencies and the surface's inhomogeneity, grain boundaries, and impurities [35]. Figure 6 displays the equivalent circuit used to fit the EIS spectra for 304 stainless in 1 M HCl in the presence and in the absence of PPO. The equivalent circuit contains (R_{ct}), (R_s), and (CPE). The impedance Z_{CPE} can be assessed from the following equation (8) [36]:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \quad (9)$$

where Y_0 is the admittance of the CPE, j is the imaginary number, ω is the angular frequency and n is the CPE exponent defined as phase shift.

Figure 5. The Nyquist (a) and Bode (b) plots for SS 304 in 1 M HCl with and without various concentrations of PPO-1 at 25°C.

Figure 6. Equivalent electrical circuit utilized to fit the impedance data.

The data of n exponent (Table 5) vary from 0.770 to 0.876 that are representative of non-ideal capacitive behavior, which is assigned to the heterogeneity of 304 stainless surfaces due to the surface roughness [36, 37].

Table 5 reports the EIS parameters. Increasing the concentration of the PPO raises the (R_{ct}) owing to an increase in the thickness of the adsorbed layer and lower the (C_{dl}) as a result of an increase in the thickness of the electrical double layer or/and a decrease in the dielectric constant due to the substitution of the adsorbed water molecules on 304 stainless steel by PPO molecules, indicating that the PPO molecules function by adsorption at the 304SS/interface [38]. The order of %IE for PPO is: PPO-1 > PPO-2 > PPO-3, which agrees with the results obtained from WL and PP experiments.

Table 5. EIS parameters for SS 304 in 1 M HCl in the absence and in the presence of various concentrations of PPO derivatives at 25°C.

Concentration, μM	R_s , Ω·cm ²	R_{ct} , kΩ·cm ²	Y_0 , μΩ·s ^{<i>n</i>} cm ⁻²	<i>n</i>	C_{dl} , μFcm ⁻²	θ	%IE	
blank	0.88	165.6	382.7	0.872	254.9	—	—	
PPO-1	4	0.66	484.6	293.0	0.795	177.0	0.658	65.8
	8	0.87	534.5	187.3	0.811	109.5	0.690	69.0
	12	0.98	707.9	160.6	0.801	93.4	0.766	76.6
	16	0.94	929.4	151.2	0.781	87.3	0.822	82.2
	20	0.92	1187.0	98.0	0.815	60.0	0.860	86.0
	24	0.70	1812.0	54.5	0.781	28.5	0.909	90.9
PPO-2	4	1.13	380.0	261.0	0.875	187.5	0.564	56.4
	8	0.93	447.1	203.4	0.876	145.0	0.630	63.0
	12	0.95	584.5	155.3	0.795	83.5	0.717	71.7
	16	1.02	608.2	142.0	0.799	76.5	0.728	72.8
	20	0.99	726.9	104.5	0.802	55.4	0.772	77.2
	24	1.13	1051.0	97.3	0.770	49.3	0.842	84.2
PPO-3	4	0.91	325.6	291.7	0.861	199.7	0.491	49.1
	8	1.05	383.70	184.7	0.842	112.6	0.568	56.8
	12	0.81	414.10	156.1	0.871	104.0	0.600	60.0
	16	0.95	519.50	153.1	0.832	91.9	0.681	68.1
	20	1.30	541.00	129.5	0.818	71.5	0.694	69.4
	24	1.54	663.80	98.7	0.834	57.3	0.751	75.1

Electrochemical frequency modulation (EFM)

The EFM technology is fast and nondestructive. The i_{corr} , causality factors CF-2 and CF-3, and Tafel slopes (β_a and β_c) were determined from the higher peaks. The data obtained from EFM for 304 stainless 1 M HCl with various concentrations of PPO at 25°C were assessed and are recorded in Table 6. The data show that i_{corr} decrease with an increase in the concentration of PPO while the %IE increases. The CF (causality factors) are close to their theoretical values [39, 40]. The %IE can be calculated as in Equation 2. The spectra achieved from EFM in the absence and in the presence of various concentrations of PPO-1 are displayed in Figure 7. EFM data are in excellent agreement with the results obtained through the other electrochemical tests. The order of inhibition proficiency for PPO compounds is PPO-1>PPO-2>PPO-3, which agrees with the results obtained from WL, PP, and EIS experiments.

Table 6. Electrochemical parameters obtained by EFM technique for SS 304 in 1 M HCl without and with different concentrations of PPO derivatives at 25°C.

Conc., mM	i_{corr} , $\mu\text{A cm}^{-2}$	b_a , mV/decade	$-b_c$, mV/decade	C.R., mpy	CF-2	CF-3	θ	%IE
blank	98.04	85.1	94.9	44.77	2.417	2.670	–	–
PPO-1	4	35.03	80.0	15.99	1.814	3.123	0.643	64.3
	8	30.50	84.1	13.90	1.973	2.895	0.689	68.9
	12	25.02	81.8	11.42	1.602	2.806	0.745	74.5
	16	23.01	62.8	77.5	1.895	3.014	0.765	76.5
	20	13.03	75.2	94.2	1.770	2.951	0.867	86.7
	24	9.48	77.9	101.0	1.833	3.031	0.903	90.3
PPO-2	4	41.27	70.8	18.85	2.170	3.014	0.579	57.9
	8	35.44	75.5	111.7	1.862	2.984	0.639	63.9
	12	31.31	81.7	112.3	1.918	3.011	0.681	68.1
	16	28.22	80.1	108.3	1.944	3.035	0.712	71.2
	20	25.55	75.1	103.2	1.956	3.068	0.739	73.9
	24	19.37	76.2	97.2	1.862	3.025	0.802	80.2
PPO-3	4	51.28	84.2	106.0	1.982	3.040	0.477	47.7
	8	45.59	78.5	103.8	1.968	2.950	0.535	53.5
	12	39.01	82.3	125.7	1.974	2.770	0.602	60.2
	16	36.01	77.5	107.1	1.750	2.860	0.633	63.3
	20	33.06	74.7	106.5	1.984	3.020	0.663	66.3
	24	26.03	78.1	125.1	1.845	3.018	0.734	73.4

Surface analysis

Figure 8a–e displays the 2D and 3D AFM morphology for 304 stainless surfaces before and after immersion in 1 M HCl in the absence and in the presence of $24 \cdot 10^{-6}$ M of PPO compounds. Figure 8a shows that the AFM image of polished 304 stainless surfaces (bare metal) seems smooth, with a small roughness (28.22 nm). Immersion in HCl (blank) for 24 h results in dissolution and the roughness of 304 stainless rises (382.86 nm) as shown in Figure 8b. After 24 h of dissolution, no pitting was detected on the 304 stainless steel in the presence of $24 \cdot 10^{-6}$ M of PPO, and the surface roughness decreased (92.41, 164.18, 180.67 nm) in comparison with the blank sample as demonstrated in Figure 8c–e. The 304 stainless coins are smoothed by the adsorbed surface layers of the PPO [41].

Figure 7. EFM graphs for SS 304 in 1 M HCl with and without various concentrations of PPO-1 at 25°C.

Quantum chemical calculations (QM)

The relationship between the molecular structure of PPO and its protective action was described via QM. Table 7 demonstrates the quantum chemical parameters calculated for PPO molecules, particularly E_{LUMO} , E_{HOMO} , ΔE , and μ . Figure 9 demonstrates the optimized structure, HOMO, and LUMO for PPO molecules.

The HOMO of PPO molecules is mostly located on N, O, and phenyl pyrazolidine moiety, which favors the electron-donating from PPO molecules to the 304 stainless (Figure 9). PPO-1 has the highest E_{HOMO} , hence, the best corrosion inhibition action was shown by PPO-1 (−4.496 eV) compared with PPO-2 (−4.986 eV) and PPO-3 (−5.118 eV). Generally, the smaller the ΔE value, the more simple it is to donate electrons and the better the adsorption on 304 stainless steel surface [42]. Therefore, the lowest ΔE value for PPO-1 molecule (1.305 eV) favors the adsorption and improves the %IE (Table 7).

Table 7 demonstrates the highest dipole moment for PPO-1 molecule (9.667 Debye), which indicates an IE rise [43–45]. Additionally, the PPO-1 molecule has the highest surface area (397.269 Å²), which raises the interaction area among the PPO-1 molecule and the

surface of 304 stainless steel or increases the area of 304 stainless steel coated with a molecule.

2D

(a) Free

3D

(a) Free

(b) 1 M HCl

**(c) 1 M HCl + 24·10⁻⁶ M
PPO-1**

(b) 1 M HCl

**(c) 1 M HCl + 24·10⁻⁶ M
PPO-1**

**(d) 1 M HCl + 24·10⁻⁶ M
PPO-2**

**(e) 1 M HCl + 24·10⁻⁶ M
PPO-3**

**(d) 1 M HCl + 24·10⁻⁶ M
PPO-2**

**(e) 1 M HCl + 24·10⁻⁶ M
PPO-3**

Figure 8. 2D and 3D AFM images of the SS 304 surface (a) before exposure in 1 M HCl solution, (b) after immersion in 1 M HCl for 24 h, and (c–e) after immersion in 1 M HCl with addition of 24·10⁻⁶ M of PPO derivatives for 24 h at 25°C.

Figure 9. The HOMO and LUMO of the PPO molecules using DMol³.

Table 7. The calculated quantum chemical parameters for PPO derivatives utilizing DMol³.

	PPO-1	PPO-2	PPO-3
E_{HOMO} , eV	−4.496	−4.986	−5.118
E_{LUMO} , eV	−3.191	−2.87	−2.935
$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, eV	1.305	2.116	2.183
Dipole moment, Debye	9.667	5.296	4.572
Molecular surface area, Å ²	397.269	322.300	315.066

Mechanism of inhibition

Based on the results obtained from chemical and electrochemical studies, the protection mechanism of PPO could be assumed. The examined PPO molecules can be converted to a cation (protonated form) in an acid medium. The protonated PPO molecules have various active centers, which are the N, O atoms, and π -orbitals of benzene [46]. Hence, the inhibitive properties of the PPO may be achieved by the contribution of two types of interaction: (a) Electrostatic attraction (physical adsorption) between the protonated PPO particles (positive charge) and the cathodic destinations of SS surface (negative charge). Furthermore, electrostatic association between the Cl⁻ particles (negative charge) and the anodic destinations of SS surface (positive charge), (b) Chemical attraction (chemisorption) between the N⁺ molecule and π -orbitals of benzene rings, unpaired electrons of N, O atoms, and the vacant d-orbitals of iron surface molecules. In this way, using multiple sites of adsorptions, PPO molecules can adhere strongly to 304 stainless steel surface [46]. These methods of association are consistent with the estimated ΔG_{ads}^0 values, hence PPO undergoes chemisorption.

Conclusions

Based on the experimental and theoretical results, we can assume that the PPO derivatives are good inhibitors for the protection of 304 stainless steel from dissolution in the acid environment. Furthermore, the %IE of PPO derivatives raises with concentration and the PPO molecules adsorbed on the surface of 304 stainless steel diminish the C_{dl} values in the presence of the PPO derivatives in comparison with a blank solution, as also confirmed by AFM tests. Moreover, the adsorption of the PPO derivatives on 304 stainless steel in 1 M HCl is found to be chemisorption and is described by the Langmuir isotherm. Finally, the %IE for 304 stainless steel surfaces utilizing PPO derivatives in 1 M HCl is confirmed by both experimental and theoretical approaches.

Funding

This research received no external funding.

Conflicts of Interest

The authors declare no conflict of interest.

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