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Synergistic effect of potassium iodide with (E)-3-(4 methoxystyryl)quinoxalin-2(1H)-one on the corrosion inhibition of carbon steel in 1.0 M HCl

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ABSTRACT

The effects of (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) and its synergistic effect with KI on the corrosion of carbon steel in 1.0 M HCl solution were studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The inhibition efficiency increases with the concentration of the inhibitor and increased further with the presence of 1.0 mM KI. The synergistic effect of 1.0 mM KI at different concentrations of Q1 was determined by calculating the synergism parameters. EIS plot indicates that the addition of inhibitor increases the charge-transfer resistance (R_{ct}) and decreases the double-layer capacitance (C_{dl}) of the corrosion process. The adsorption of Q1 and KI on the metal surface in 1.0 M HCl solution obeys the Langmuir adsorption isotherm.

Keywords: Carbon steel, quinoxalinones, HCl, Synergistic effect, Polarisation curves, EIS.

INTRODUCTION

Carbon steel is used in mass amounts in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment [1-4], despite it has a relatively high cost. These applications usually induce serious corrosive effects on equipment's, tubes and pipelines made of iron and its alloys [5-7]. The use of corrosion inhibitors is one of the most effective measures for protecting metal surfaces against corrosion in acidic environments [8-26]. Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. A literature survey shows that most of the organic inhibitors will act upon adsorption onto the metal surface. The adsorption of inhibitors takes place through hetero-atoms such as nitrogen, oxygen, phosphorus, and sulfur, as well as through triple bounds or aromatic rings. The inhibition efficiency is reported to increase in the order O < N < S < P [27].

Synergism is an effective method to improve the inhibitive action of an inhibitor in presence of another substance in corrosive medium and to decrease amount of usage [28]. The addition of halide salts to some inhibitor solution results in synergistic effect. Recently, several studies have been reported to explain role of synergism on corrosion inhibition mechanism of steel in sulphuric acid (H_2SO_4) medium [29-31]. This synergism is due to increased surface coverage as a result of ion-pair interactions between organic cation and halide anion. The halide ions present in an inhibiting solution adsorb on corroding electrode surface by creating oriented dipoles and facilitates the adsorption of inhibitor cations on the dipoles [30]. The synergistic effect of different halide ions with pyrazoles on corrosion of low carbon steel in H_2SO_4 have been reported [32]. The inhibitive effect of halide ions found to be in the order $I^- > Br^- > Cl^-$. Jeyaprabha et al. [31] reported the highest synergistic effect of iodide ions is due to its chemisorption with metal surface and its larger size and low electronegativity. The synergistic action of iodide ions with polyacrylamide on corrosion of steel in aerated sulphuric acid [33] with dodecylamine on corrosion of cold rolled steel in 0.1 M phosphoric acid [34] and with some aliphatic amines on corrosion of carbon steel in sulphuric acid [35] are reported. Most of the existing literature reported the synergism order as $I^- > Br^- > Cl^-$ but in some cases the change in synergism order $I^- < Br^- < Cl^-$ has also been reported [32]. Mu et al. [36,37] explained the synergism between Tween-60 and sodium chloride on corrosion of cold rolled steel in 0.5 M H_2SO_4 and also the combined effect of o-phenanthroline and chloride ion on cold rolled steel in phosphoric acid. In other hand, the synergistic effect of halide ions played an important role in controlling corrosion rate of other metals also. Ebenso [38] studied the synergistic effect of halide ions on corrosion inhibition of aluminium in sulphuric acid in presence of 2-acetylphenothiazine and the effect of KI on copper corrosion inhibition in presence of 2-mercaptobenzimidazole in aerated sulphuric acid solution was investigated by Zhang et al. [39].

To our surprise, neither the inhibiting ability of (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) (Fig. 1) nor the synergistic effects with iodide ions toward the acid corrosion of carbon steel have been previously studied. In the present a new corrosion inhibitor, (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) and KI, have been investigated their inhibition effect on the corrosion of carbon steel in 1.0 M HCl solutions by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Then, we attempted to enhance inhibition efficiency synergistically further by the addition of KI to Q1 molecules containing corrosive solution.

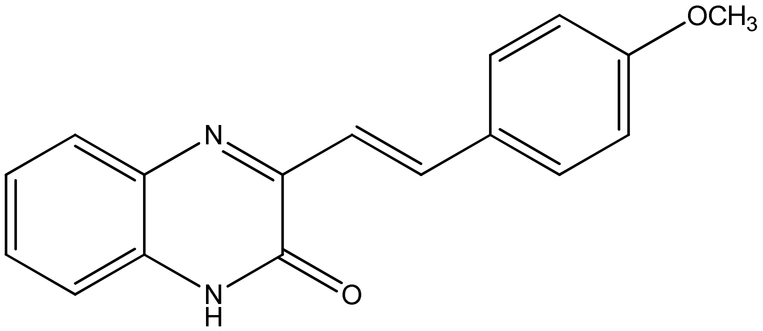


Figure 1. The chemical structure of studied compound

MATERIALS AND METHODS

Materials

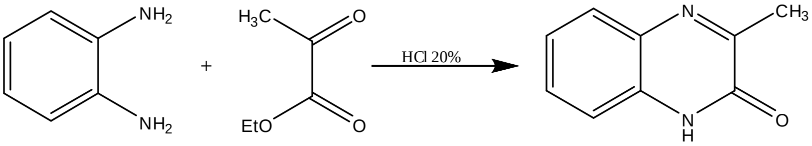
The steel used in this study is a carbon steel (CS) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe).

Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) used was 10^{-8} M to 10^{-5} M with 1.0 mM KI.

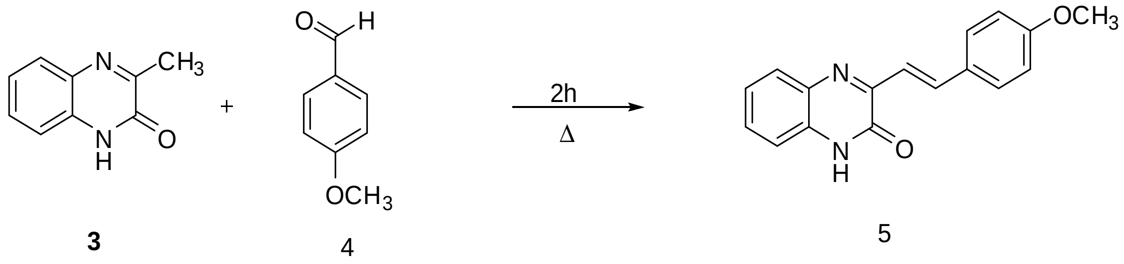
Synthesis

Inhibitors studied are synthesized in our laboratory according to the procedure described in the schemes 1 and 2. In the literature, 3-methylquinoxalin-2-one is prepared according to Philip's method [40] (scheme 1)



Scheme 1. Synthesis of 3-methylquinoxalin-2-one

The bibliography reports various methods to prepare styrylquinoxalines [41,42]. For our part, we suggested a different synthetic route which comprises reacting fusion3- méthtylquinoxaline-2-one with aromatic aldehydes. This method, carried out in the absence of solvent, we have a possibilityto isolate the desired compound in a yield of around 80% (Scheme 2). Indeed, 6.25 mmol of 3-méthylquinoxalin-2-one is fused with 12.5 mmol of the appropriate aldehyde for 2 hours at the boiling temperature of the latter. At the end of the reaction, the solid compound is allowed to cool and then heated at 100 ° C for 10 minutes in 50 ml of ethanol. The product is filtered hot then washed with ethanol [43].



Scheme 2. Synthesis of 3-methylquinoxalin-2-one

Polarization measurements

Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using Volta lab (Tacussel-Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Volta master 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 1 cm^2. The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp}, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 303 K. The EIS experiments were conducted in the frequency range with high limit of 100 KHz and different low limit 10 mHz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the *x*-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation:

$$\eta_z \% = \frac{R^i_{ct} - R^\circ_{ct}}{R^i_{ct}} \times 100 \qquad (1)$$

Where, R°_{ct} and R^i_{ct} are the charge transfer resistance in absence and in presence of inhibitor, respectively.

Potentiodynamic polarization

The electrochemical behavior of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1.0 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 to 0 mV versus corrosion potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). From the polarization curves obtained, the corrosion current (I_{corr}) was calculated by curve fitting using the following equation:

$$I = I_{corr}\left[exp\left(\frac{2.3\Delta E}{\beta_a}\right) - exp\left(\frac{2.3\Delta E}{\beta_c}\right)\right] \qquad (2)$$

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta_{Tafel} \% = \frac{I^\circ_{corr} - I^i_{corr}}{I^\circ_{corr}} \times 100 \qquad (3)$$

Where, I°_{corr} and I^i_{corr} are the corrosion current density in absence and presence of inhibitor, respectively.

RESULTS AND DISCUSSION

Electrochemical impedance spectroscopy

The corrosion response of carbon steel in 1.0 M HCl in the presence of various concentrations of inhibitor and inhibitor + 1.0 mM KI systems has been investigated using Electrochemical Impedance Spectroscopy at 303 K. Figures 2 and 3 represent the Nyquist plots of carbon steel specimens in 1.0 M HCl in the presence of various concentrations of inhibitor and inhibitor + 1.0 mM KI, respectively. It is evident from the plots that the impedance response ofmetal specimens has marked difference in the presence and absence of the KI with inhibitor Q1.

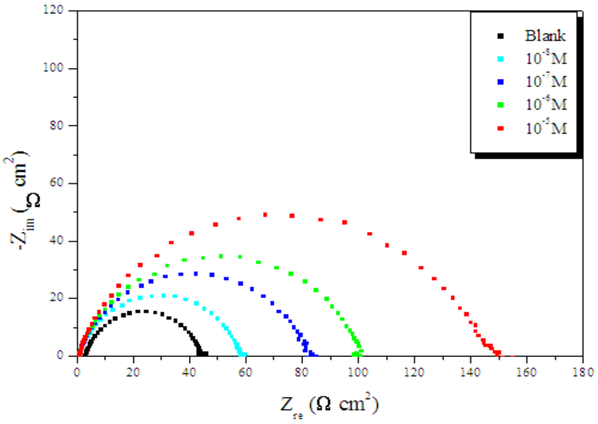


Figure 2. Nyquist plots for carbon steel in 1.0 M HCl containing various concentrations of Q1 at 303 K

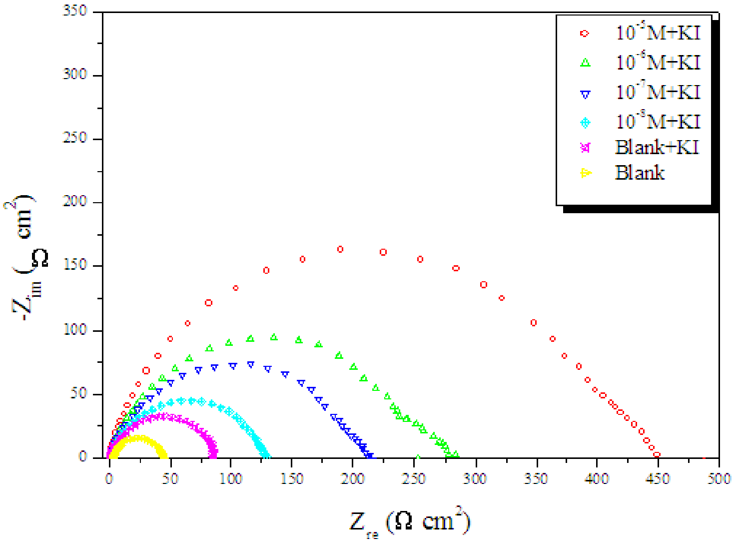


Figure 3. Nyquist plots for carbon steel in 1.0 M HCl with and without various concentrations of Q1 and 10^{-3}M KI at 303K

Impedance behaviour can be well explained by pure electric models that could verify and enable to calculate numerical values corresponding to the physical and chemical properties of electrochemical system under examination [44]. The simple equivalent circuit that fit to many electrochemical systems composed of a double layer capacitance, R_s and R_{ct} [45, 46]. To reduce the effects due to surface irregularities of metal, constant phase element (CPE) is introduced into the circuit instead of a pure double layer capacitance which gives more accurate fit as shown in the Figure 4 [47].

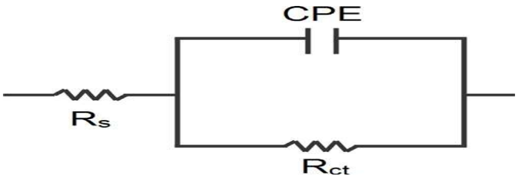


Figure 4. Equivalent circuit fitting for EIS measurements

The impedance of CPE can be expressed as

$$Z_{CPE} = \frac{1}{Y_0 \left(j\omega \right)^n} \qquad (4)$$

where Y_0 is the magnitude of CPE, n is the exponent (phase shift), ω is the angular frequency, and j is the imaginary unit. CPE may be resistance, capacitance, and inductance depending upon the values of n [48]. In all experiments the observed value of n ranges between 0.82 and 0.93, suggesting the capacitive response of CPE. The EIS parameters such as R_{ct}, R_s, and CPE and the calculated values of percentage of inhibition (η_z%) of carbon steel specimens are listed in Table 1.

Table 1. Impedance parameters for carbon steel in 1.0 M HCl at different concentrations of Q1 in the presence and absence of 10^{-3}M KI at 303K

[Q1] (M)	[KI] (M)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	η_z (%)
Blank	—	41	154	—
—	10^{-3}	85	74	52
10^{-5}	—	147	68	72
—	10^{-3}	411	24	90
10^{-6}	—	102	78	57
—	10^{-3}	250	32	84
10^{-7}	—	83	96	47
—	10^{-3}	206	62	80
10^{-8}	—	58	137	24
—	10^{-3}	127	63	67

From Table 1 it is clear that R_{ct} values are increased with increasing inhibitor concentration. The capacitance values C_{dl} decreases with inhibitor concentration and this decrease in C_{dl} is enhanced upon addition of I^- ions to the corrosive environment (inspect data listed in Table 1). These results suggest that the Q1 molecules function by adsorption at the metal/solution interface [49] and this adsorption is reinforced by I^- ions. This decrease in C_{dl} may be explained on the basis that the double layer between the charged metal surface and the solution is considered as an electrical capacitor. The η_z% data reveal that the corrosion inhibition capacity of Q1 is markedly enhanced by the addition of KI.

Tafel polarization measurements

The potentiodynamic polarization curves of carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of Q1 and Q1/KI mixture are shown in Figs. 5-6, respectively. The values of related electrochemical parameters, i.e. corrosion current density (I_{corr}), E_{corr} (vs. SCE), cathodic Tafel slope (β_c) and the inhibition efficiency (η_{Tafel}) deduced from the polarization curves are summarized in Table 2.

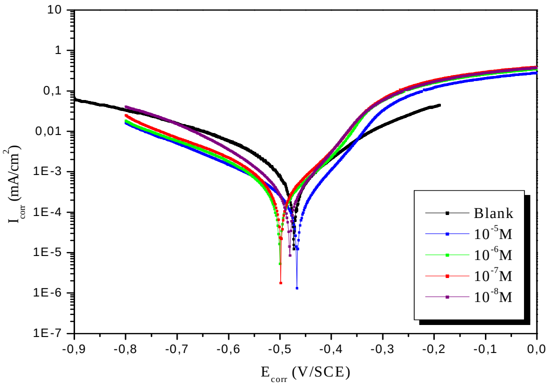


Figure 5. Polarisation curves of carbon steel in 1.0 M HCl without and with different concentrations of Q1 at 303 K

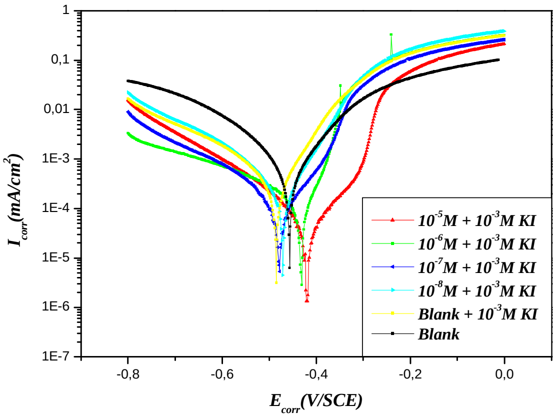


Figure 6. Potentiodynamic polarization curve for carbon steel in 1.0 M HCl with and without various concentrations of Q1 and 10^{-3}M KI at 303 K

The corrosion current densities were obtained by the extrapolation of the current-potential lines to the corresponding corrosion potentials. Herein, the corrosion rates were calculated assuming that the whole surface of carbon steel is attacked by corrosion and no local corrosion is observed.

As it can be clearly seen from Fig. 5 that, the addition of Q1 to the corrosive solution both reduces anodic dissolution of iron and also retards cathodic hydrogen evolution reactions. The corrosion current density of steel considerably reduced in the presence of the Q1 and the inhibition efficiency η_{Tafel} is more and more pronounced with the increasing Q1 concentration. These results are indicative of the adsorption of Q1 molecules on the carbon steel surface.

Inspection of Table 2 reveals that the corrosion potential (E_{corr}) of Q1 and Q1/KI mixture shifted to positive values in comparison with corrosion potential observed in blank solution, but these shifts are not enough to decide it cathodic or anodic inhibitor, i.e. Q1 and Q1/KI mixture act as mixed-type inhibitor [50,51]. Fig. 6 shows the polarization curves for carbon steel in 1.0 M HCl containing various concentrations of Q1 and 1.0 mM of KI at 303 K. It is apparent that I_{corr} decreases considerably in the presence of iodide ions, and decreases with increasing the inhibitor concentration. Correspondingly, η_{Tafel} increases with the inhibitor concentration, due to the increase in the blocked fraction of the electrode surface by adsorption. According to data of Table 2, the corrosion current density decreases substantially, leading to higher inhibition efficiency of Q1/KI mixture, up to 92%, compared to 72% obtained for alone 10^{-5} M of Q1. This indicates a synergistic inhibition effect between Q1 and KI [52].

Table 2. Potentiodynamic electrochemical parameters for carbon steel in 1.0 M HCl at different concentrations of Q1in the presence and absence of 10^{-3}M KI at 303K

[Q1] (M)	[KI] (M)	β_c (mV/dec)	E_{corr} (mV_{SCE})	I_{corr} ($\mu A\ cm^{-2}$)	η_{Tafel} (%)
Blank	—	93	474	442	—
—	10^{-3}	192	489	220	50
10^{-5}	—	99	471	125	72
—	10^{-3}	95	438	35	92
10^{-6}	—	80	504	169	62
—	10^{-3}	72	452	65	85
10^{-7}	—	76	502	182	59
—	10^{-3}	92	430	80	82
10^{-8}	—	79	486	197	55
—	10^{-3}	100	431	145	67

Adsorption Isotherm and Free Energy of Adsorption

Adsorption isotherm calculation of the (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) on the carbon steel surface in the presence and absence of halide ions were performed to investigate the mode of adsorption. Surface coverage values (θ) (defined as $\theta = \%\eta_{Tafel}/100$) were evaluated from η_{Tafel} obtained from potentiodynamic as well as EIS measurements in order to yield the best fit isotherm model [53]. In order to study the different types of adsorption isotherm models, the Temkin, Freundlich, Frumkin and Langmuir models have been plotted. This indicated that the data does not follow the Temkin, Freundlich or Frumkin adsorption isotherm model. According to the R^2 values obtained from the linear graph, it was confirmed that the adsorption of Q1 on a carbon steel surface best fitted the Langmuir adsorption isotherm model which is represented by Eq. (5).

$$\frac{\theta}{1-\theta} = KC \qquad (5)$$

By rearranging this equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

where C is the inhibitor concentration, K is the adsorption equilibrium constant and θ is the surface coverage. Fig. 7 shows the plots of C/θ versus C and the expected linear relationship is obtained for Q1 and Q1/KI.

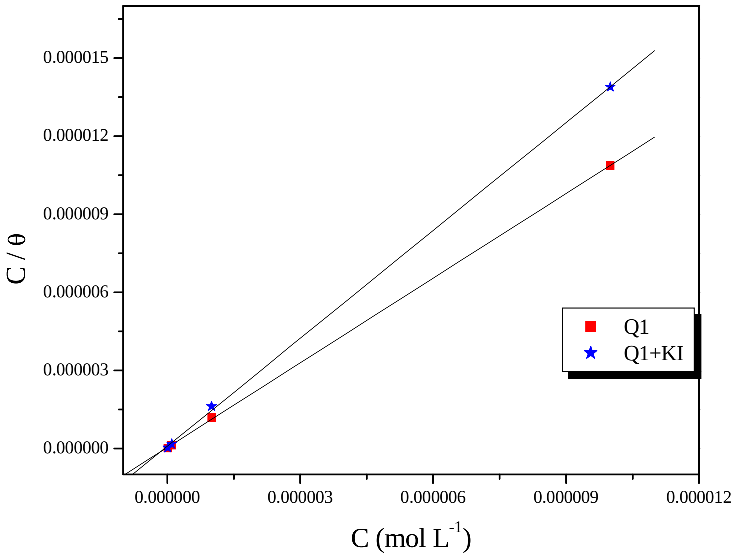


Figure 7. Adsorption isotherms for carbon steel in 1.0 M HCl in different concentrations of Q1 in the absence and the presence of 10^{-3}M KI at 303K

The standard free energy of adsorption (ΔG°_{ads}) can be given as the following equation:

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \qquad (7)$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K), the value 55.5 is the concentration of water in solution expressed in M.

The parameter values obtained and calculated from the plot are given in Table 3.

The high value of K shows that Q1 is strongly adsorbed on the carbon steel surface in presence of KI [54]. The value of K in absence of KI is lower than the value of K in presence of KI, this indicates that the Q1 molecules were strongly adsorbed on the carbon steel surface in presence of KI; this was due to the synergistic effect of KI. The obtained values of ΔG°_{ads} are negative. The negative values ensure the spontaneity of the adsorption process and the stability of adsorbed layer on the carbon steel surface. Values of ΔG°_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged inhibitor molecules and the charged metal surface (physisorption); those around -40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [55]. The calculated ΔG°_{ads} values were -51.15 and -53.38 kJ mol^{-1} for the adsorption of Q1 in absence and presence of KI, respectively. This indicates that the adsorption takes place mainly through the donor-acceptor bond between unpaired electrons of Q1 and Q1+KI and the active centers of the carbon steel surface (chemisorption) [56].

Table 3. Thermodynamic parameters for the adsorption of Q1 and Q1+1.0 mM KI in 1.0 M HCl on the carbon steel at 303 K

Inhibitor	K_{ads} (M^{-1})	R^2	ΔG°_{ads} (kJ/mol)
Q1	11875469.08	0.99997	-51.15
Q1+KI	28689794.47	0.99988	-53.38

Synergistic inhibition effect of iodide ions

It is generally observed that the addition of halide ions to the corrosive media increases the adsorption ability of organic cations by forming interconnecting bridges between negatively charged metal surface and inhibitor cations. The order of synergism of halide ions is $I^- > Br^- > Cl^-$. This due to the iodide ions has large ionic radius, high hydrophobicity and easy polarizability more than bromide and chloride ions [57,58].

The synergistic inhibition effect of inhibitors takes place when the total action of compounds is higher than the sum of each one individually. The synergism parameters (S) were calculated and listed in Table 4, using the following equation [59]:

$$S = \frac{1-(\eta_1+\eta_2)}{1-\eta_{1+2}} \qquad (8)$$

where η_1 is the inhibition efficiency of iodide ions, η_2 is the inhibition efficiency of the inhibitor and η_{1+2} is the inhibition efficiency of iodide + inhibitor mixture.

Table 4. Synergism parameters of carbon steel in 1.0 M HCl solution at 303 K

Inhibitor	Tafel		EIS	
	η_{Tafel} (%)	S	η_z (%)	S
1.0 mM KI	50	—	52	—
10^{-5} M Q1	72	—	72	—
10^{-6} M Q1	62	—	57	—
10^{-7} M Q1	59	—	47	—
10^{-8} M Q1	55	—	24	—
10^{-5} M Q1+ 1.0 mM KI	92	1.33	90	1.38
10^{-6} M Q1 + 1.0 mM KI	85	1.32	84	1.30
10^{-7} M Q1 + 1.0 mM KI	82	1.33	80	1.24
10^{-8} M Q1 + 1.0 mM KI	67	1.58	67	1.14

It was found that the inhibition efficiency for solutions with KI exhibit higher values compared to solutions without KI, This reflects that KI has a synergistic inhibitive effect on the carbon steel corrosion in 1.0 M HCl solution. This can be explained by the strong chemisorption of iodide ions on the metal surface [60].

The (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) molecules are then adsorbed by columbic attraction on the metal surface. Stabilization of the adsorbed iodide ions with the inhibitor leads to greater surface coverage and thereby greater inhibition [61]. The iodide ions enhance the stability of the inhibitor on the metal surface by a co-adsorption mechanism, which may be either be competitive or cooperative [62]. For competitive adsorption, the anions and the inhibitor cations are adsorbed at different sites on the metal surface. In cooperative adsorption, the anions are chemisorbed on the metal surface and the cations are adsorbed on a layer of the anions. Competitive and co-operative mechanisms may occur simultaneously in some cases [63].

Generally, values of S < 1 imply that antagonistic behavior prevails, which may lead to competitive adsorption, whereas S > 1 indicates a synergistic effect [64]. It is noticed that all values of S were greater than unity. This may suggest that the enhanced inhibition efficiency caused by the addition of iodide ions to the (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) was only due to synergistic effect.

CONCLUSION

(E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (Q1) and KI inhibit the corrosion of carbon steel in 1.0 M HCl solution and the inhibition efficiency increases with an increase inhibitor concentration and increase further in the presence of Q1/KI mixture. Potentiodynamic polarization studies showed that the investigated inhibitors act as mixed-type. The adsorption of studied inhibitors on the metal surface in 1.0 M HCl solution obeys the Langmuir adsorption isotherm. The values of Gibbs free energy of adsorption indicated that Q1 and halide ions were adsorbed onto the carbon steel surface mainly by chemisorption mechanism. The addition of halide ions synergistically improved the inhibition performance of Q1 due to the co-adsorption effect.

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