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Evaluation of Schiff Base Complex of Copper (II) as Corrosion Inhibitor against 0.1M of Hydrochloric Acid

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ABSTRACT

A Schiff base complex of the coper was prepared [tetrakis (μ_3-2-{[1, 1-bis (hydroxymethyl)-2-oxidoethyl]imino-methyl}-phenolato)tetrakis[aquacopper(II)]] that referred as complex A then it characterized by FTIR, UV and NMR techniques. The prepared complex is evaluated as corrosion inhibitor for carbon steel alloy (C1010) in corrosive medium of 0.1M HCl at 25ºC at different concentrations i.e., (10-50) ppm. An optimal concentration is 10 ppm which gives efficiency about 52%. In order to raise the efficiency of the mentioned inhibitor, 7ppm of potassium iodide (KI) is added to the inhibitor, where the efficiency of the certain inhibitor raised its efficiency into high significant values for all concentrations of the inhibitor. The results insisted that the optimal efficiency is 88% at 40 ppm. On other hand, the effect of the temperature on the inhibition efficiency for the inhibitor when it mixed with KI is studied temperatures range of (25-55) ºC for all concentrations and the results reveals that the efficiency is reduced as temperature increased. Furthermore, the kinetic and thermodynamic functions were calculated and the results reveal that the inhibitor is physically adsorbed and obey to the Langmuir adsorption isotherm.

Keywords: Schiff base complexes; Corrosion inhibitors; Copper complexes; Carbon steel; hydrochloric acid

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INTRODUCTION

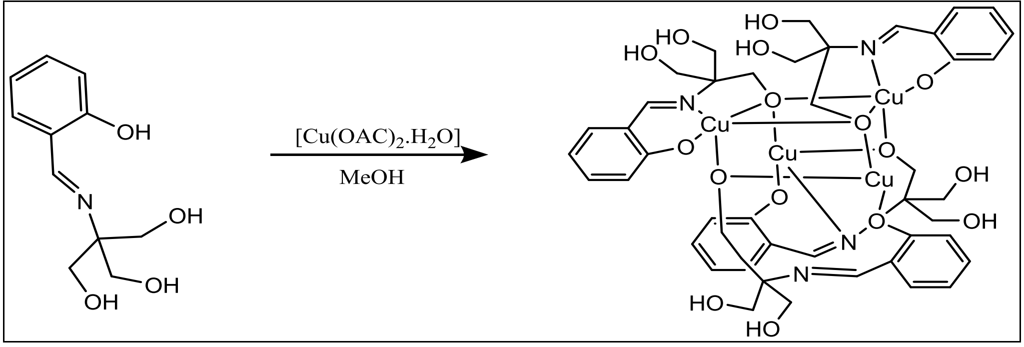
Acids like sulfuric and hydrochloric acids are commonly used for several purposes e.g., removal of undesirable scale and rust in the metal working, cleaning of boilers and heat exchangers. In fact it easily react with steel alloys to form non-protective oxides which result in gradual steel material loss and strength impoverishment. Carbon steel is among the most widely used engineering materials for more applications for instance as a metal-processing equipment, marine applications, chemical processing pipelines and so on [1-3]. However the usefulness of carbon steel as alloy is constrained by one common problem known as corrosion that can be defined is the destructive attack of a metal by chemical or electrochemical reaction with the environment [4-8]. The primary strategy is to isolate the metal or alloy from corrosive agents. One of the methods that used to protect the metals or alloys against corrosion especially in acidic environments is used the corrosion inhibitors. Compounds containing N, S and O have been reported as excellent inhibitors. The efficiency of an organic compound as an inhibitor is mainly dependent on its ability to get adsorbed on metal surface which consists of a replacement of water molecule at a corroding interface and they are influenced by their electronic structure, steric factor, aromatic, and electron density at donor site and presence of functional group such as –CHO, –N=N, R–OH, molecular area and molecular weight of the inhibitor molecule [9-17].

The growing attention toward Schiff's bases as corrosion inhibitor is due to presence of polar –CH= N- bond which act as adsorption center during adsorption of the azomethine linkage (–HC=N– group) and the donor atoms in the back bone of the Schiff bases that are responsible for their industrial application, Schiff bases, since they contain –HC=N– group, are well-known organic inhibitors of metal corrosion. Research work revealed that the inhibition efficiency of Schiff bases is much greater than that of the corresponding amines and aldehydes due to the presence of the mentioned group in the molecules [18-19]. In the present work a Schiff base complex of copper was prepared and evaluated as corrosion inhibitor for carbon steel alloy (C1010) against acidic medium of hydrochloric acid.

EXPERIMENTAL SECTION

Synthesis of Schiff base complex

The Schiff base complex of copper ion is prepared according to the procedure in reference [20]. The following equations (1-2) explain the reactions of the synthesis:



(1)

Characterization of the synthesized compounds

The complex A is characterized by FTIR, UV and NMR techniques. The stretching of frequencies at range (1587-1625) cm^{-1} and (1055-1155) cm^{-1} assigned for (-C=N-) and (-C-O-) functional groups respectively that indicate to the coordination of N atom in Schiff base or O atom in phenolic group with the central atom i.e., Cu(II) The stretching frequency at (893-910) cm^{-1}s is belong to (M-L) bond i.e., indication to the coordination between the central atom with ligand in either N and O atoms [21]. The stretching frequencies in (1585-1666) and (1510-1558) cm^{-1} is attributed to presence of aliphatic and aromatic (-C=C-) functional groups respectively [22-23]. In the UV-Visible technique revealed for complex A due to the $^2B_1 \rightarrow {}^2A_1$ transition [23]. Thus ^{1}HNMR for the complex A there are many bands at 3.35 ppm for (3H, CH_2OH), wide band at 3.62 for (6H, CH_2OH) , for aromatic protons at (6.81-8.72) ppm and wide band for 9.25 ppm for the proton of –HC=N– group (1H, imine) , on the other hand, the presence of copper ion (I=3/2) that has unpaired electrons that cause to make the relaxation time very short i.e., presence of wide bands that shield any band that can be appeared [18,24-25].

RESULTS AND DISCUSSION

Carbon steel samples preparation

In this study carbon steel strips (C1010) are used. The specimens were grinding by the silicon carbide papers by using a different grade that include; 120, 180, 320, 400 and 600 respectively. then, it was polished by polishing system with a disc that is covered by shamwa that coated by the alumina (Al_2O_3) powder where, it polished until they become like a mirror Finally, specimens washed by distilled water followed by ethanol then by acetone for 15 min then dried by the air and kept by the desiccator to keep them dry [26].

Preparation of the solutions

In this study different concentrations for the complex A is firstly prepared alone at range of (10-50) ppm and secondly each one from the same concentrations of the mentioned inhibitor is mixed with 7 ppm of potassium iodide.

Study the effect of concentration of the inhibitors at constant temperature on the inhibition efficiency

The effect of the concentration on the inhibition efficiency at range (10-50) ppm for the complex A when it presence alone and when it mixed with 7ppm of KI with the inhibitor is studied at constant temperature 25 ºC. Figures (1-4) explain Tafel plots of the carbon steel alloy in presence of A at the range of concentrations (10-50) ppm in the presence and absence of 7 ppm KI.

According to Table 1, in presence of the complex A as inhibitor, the inhibition efficiency is reduced as concentration of the inhibitor increased from 10 to 50 ppm i.e. but when, the 7ppm of KI was added for each one of the inhibitor's concentrations, the efficiency is increased at all concentrations especially at 40 ppm where, the optimal efficiency of the mentioned inhibitor is 88%.

Generally, the corrosion currents and the corrosion rate for the carbon steel alloy C(1010) is reduced in presence of the inhibitor or in presence of the mixture of the inhibitor with KI compared with the absence of the inhibitor whether it mixed with KI or not. In contrast, to the corrosion currents and the corrosion rate, the transfer charge R_{ct} is increased as these parameters are reduced On the other hand, the values of β_a and β_c is increased in presence of the inhibitor A which is meant that the mechanisms of the hydrogen evolution on the cathode and the dissolution of the anode are controlled.

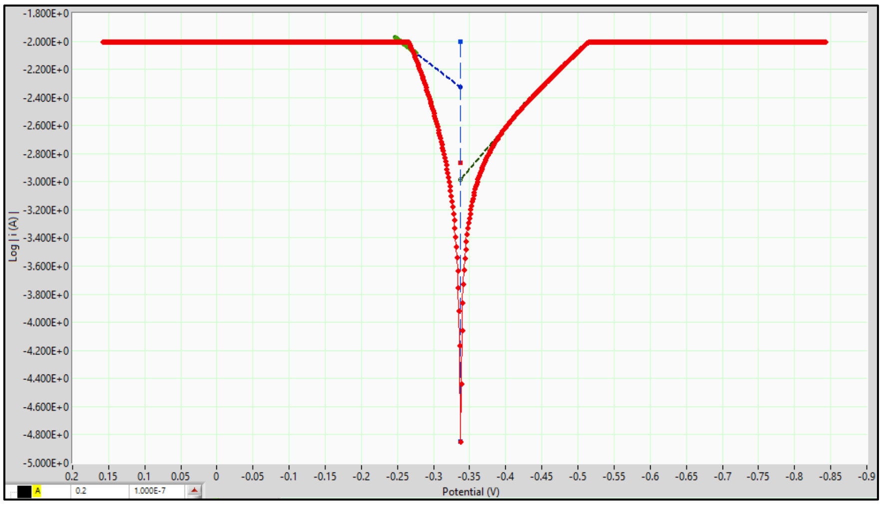


Figure 1: Tafel plot for the carbon steel alloy in presence of 0.1M HCl at 25°C

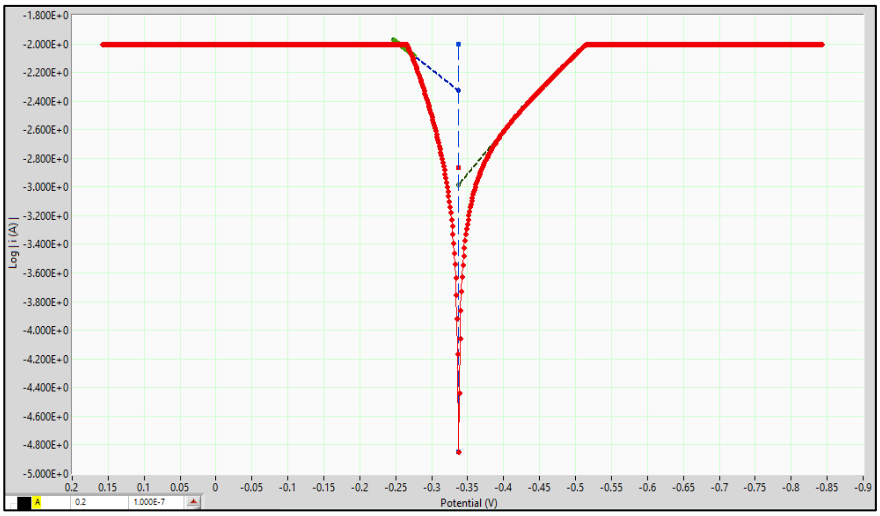


Figure 2: Tafel plot for the carbon steel alloy in presence of 7 ppm of KI against of 0.1M HCl at 25°C

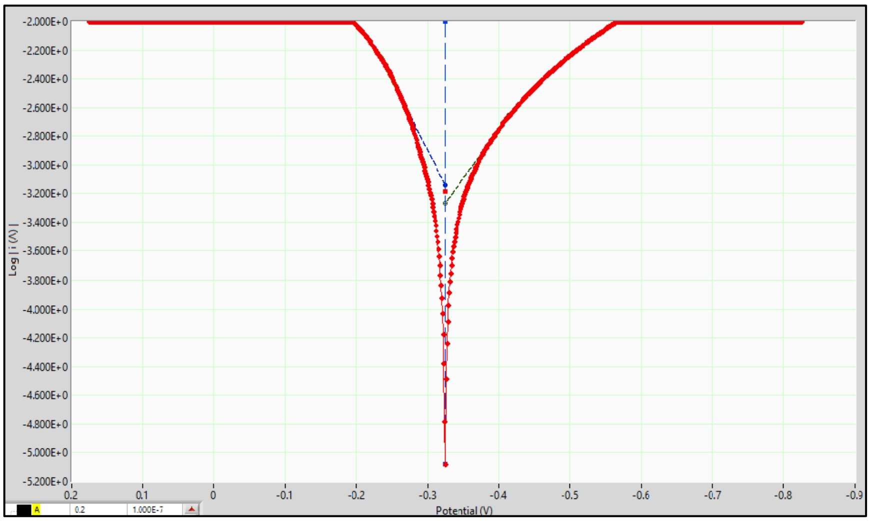


Figure 3: Tafel plot for the carbon steel alloy in presence of the optimal concentration of complex A (10ppm) against of 0.1M HCl at 25°C

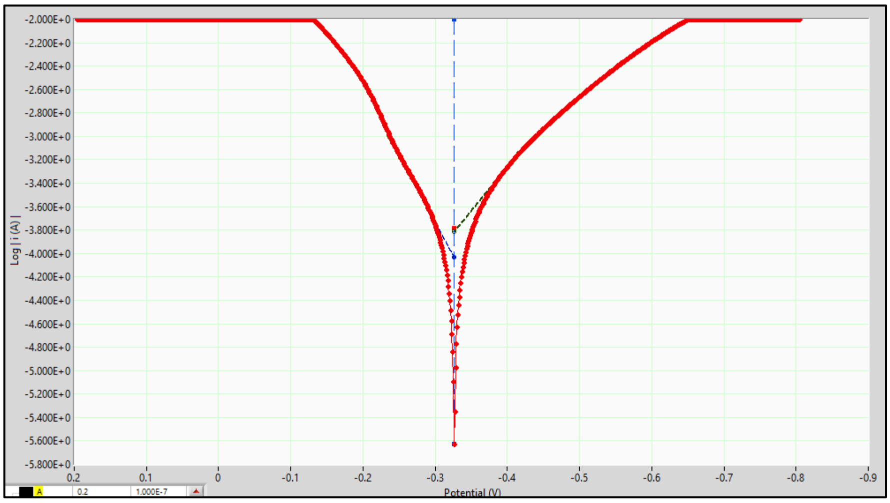


Figure 4: Tafel plot for the carbon steel alloy in presence of the optimal concentration of complex A (10ppm) with 7 ppm of KI against of 0.1M HCl at 25°C

Table 1: An electrochemical data that acquired from Tafel plot of the carbon steel alloy (C1010) at different concentrations of A at 25° C

Comp.	Conc. (ppm)	I_{corr} (μA)	CR (mpy)	E_{Corr} (V)	R_{ct} (Ω)	$β_a$ (A/V)	$β_c$ (A/V)	E %
HCl	3650	1375	75.44	-0.337	18.69	3.94	-6.07	-
A_1	10	653.6	35.86	-0.325	39.31	9.92	-6.89	52
A_1	20	819.7	44.96	-0.329	31.35	9.94	-6.77	40
A_1	30	814	44.68	-0.321	31.57	9.18	-6.76	41
A_1	40	774.3	42.48	-0.052	33.18	10.9	-6.5	43
A_1	50	740.4	40.64	-0.319	34.7	10.05	-6.83	46
A_1 + KI	10 + 7	210.1	11.52	-0.224	122.4	14.11	-7.58	85
A_1 + KI	20 + 7	185.5	10.18	-0.318	13.85	8.26	-8.09	86
A_1 + KI	30 + 7	233.9	12.84	-0.325	109.8	12.36	-7.22	83
A1 + KI	40 + 7	163.7	8.98	-0.326	156.9	11.5	-7.57	88
A1 + KI	50 + 7	205.9	11.3	-0.32	124.8	11.85	-7.02	85

Furthermore, E_{corr} values from the above Table refer to mixed inhibition behavior for this inhibitor. In fact the role of KI by the synergistic effect [26-31].

Study the effect of the temperature on the efficiency of the inhibitors at constant concentrations

The effect of temperature at range (25-55) °C on the inhibition efficiency for the inhibitor A when it mixed with KI for each one of its above concentrations. Below some of the Tafel plots for the effect of the temperature on the corrosion rate of the carbon steel alloy (C1010) are shown below in Figures (5-17) below where, the Tafel plot of the optimal concentration for the inhibitor is selected at the certain temperature:

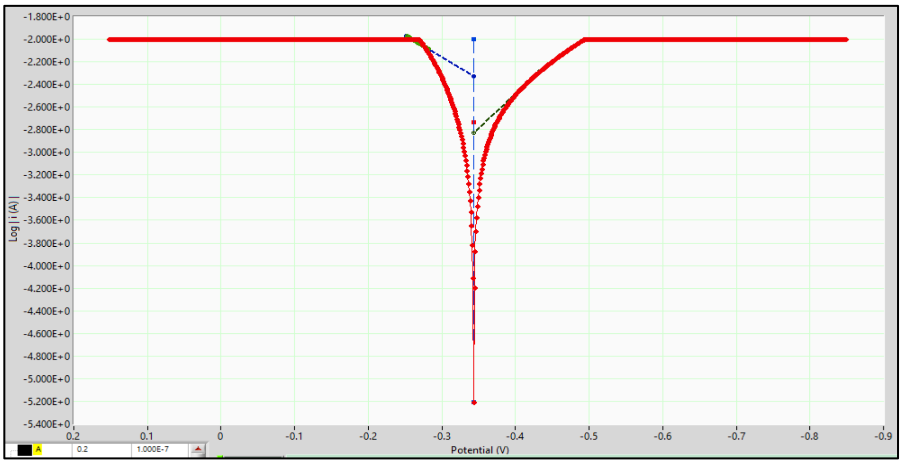


Figure 5: Tafel plot for the carbon steel alloy in presence of 0.1M HCl at 35°C

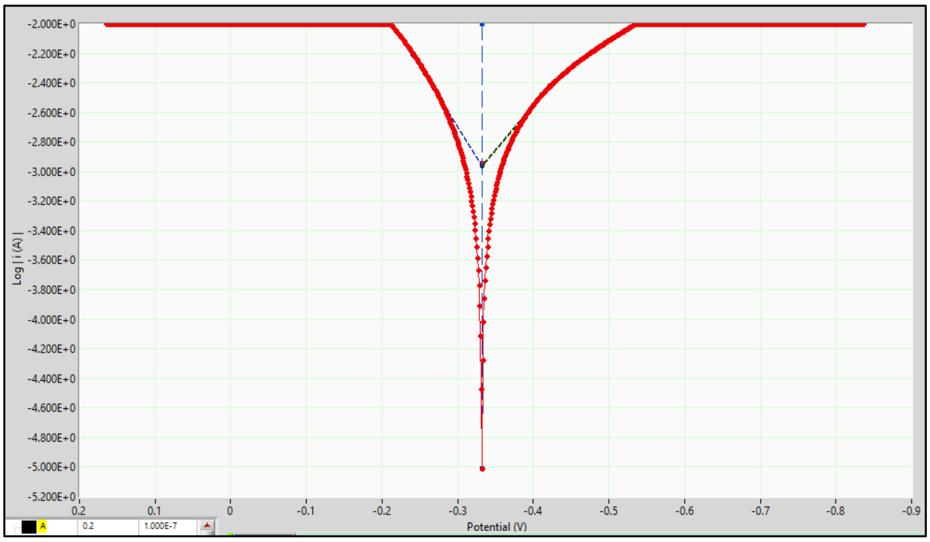


Figure 6: Tafel plot for the carbon steel alloy in presence of 7 ppm of KI against of 0.1M HCl at 35°C

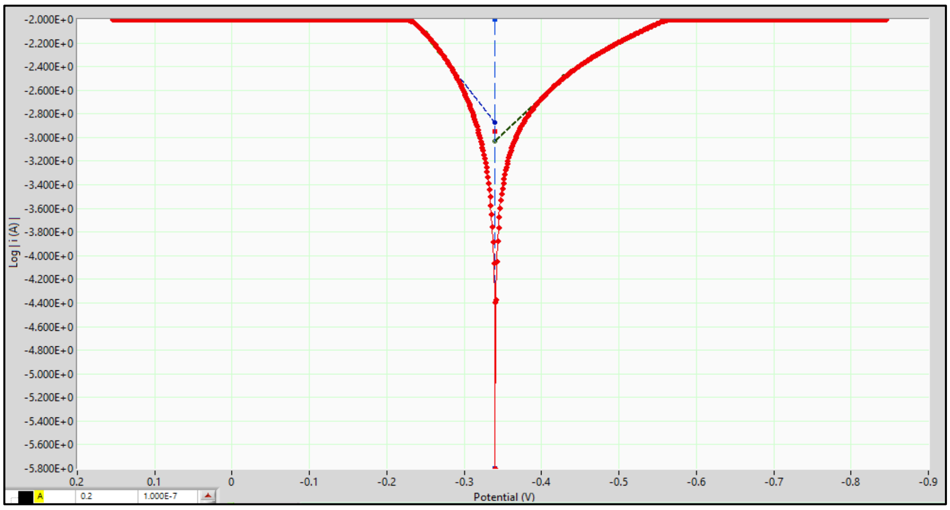


Figure 7: Tafel plot for the carbon steel alloy in presence of the optimal concentration of the complex A (30ppm) against of 0.1M HCl at 35°C

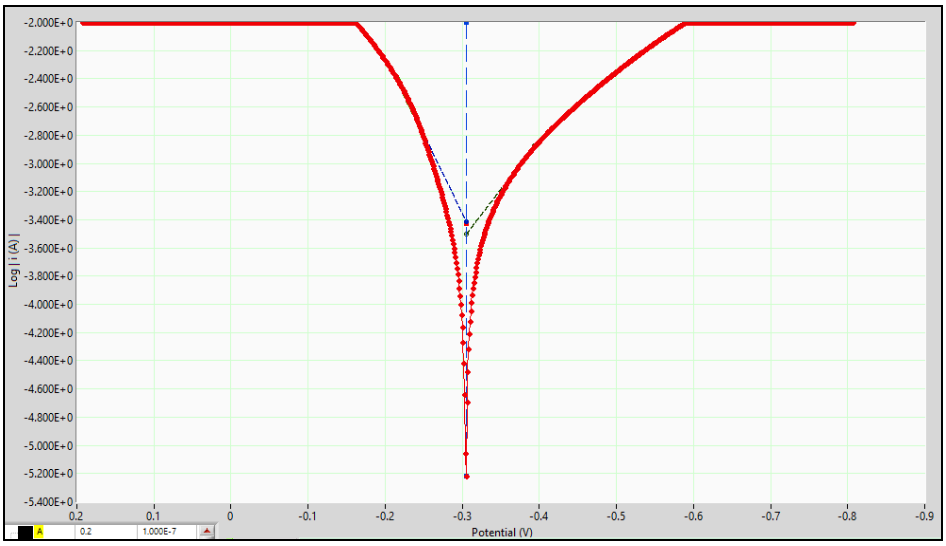


Figure 8: Tafel plot for the carbon steel alloy in presence of the optimal concentration of the complex A (30ppm) with 7 ppm of KI against of 0.1M HCl at 35°C

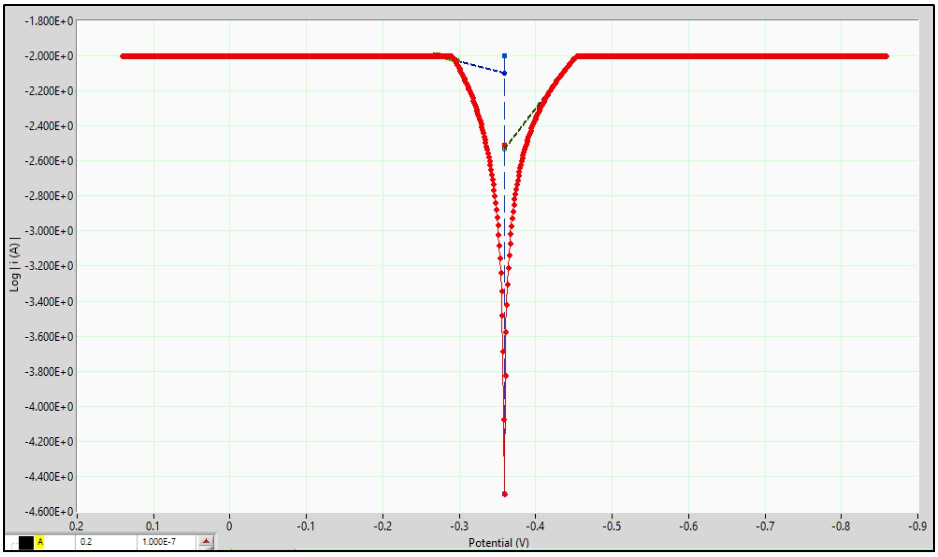


Figure 9: Tafel plot for the carbon steel alloy in presence of 0.1M HCl at 45°C

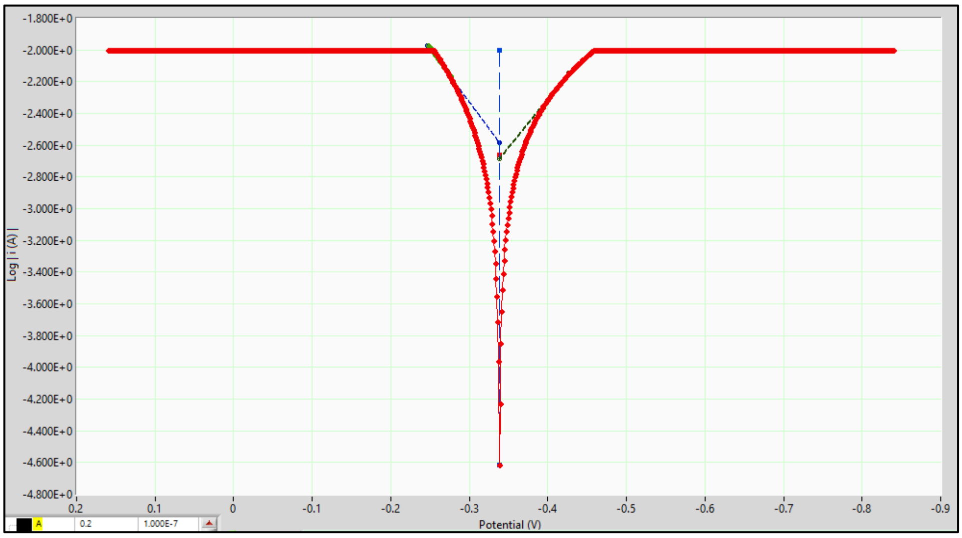


Figure 10: Tafel plot for the carbon steel alloy in presence of 7 ppm of KI against of 0.1M HCl at 45°C

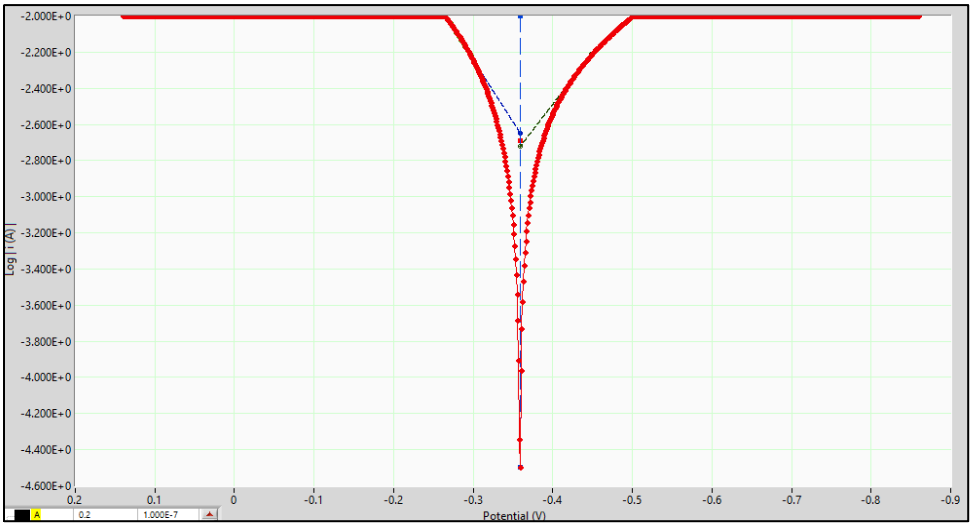


Figure 12: Tafel plot for the carbon steel alloy in presence of the optimal concentration of the complex A (10ppm) against of 0.1M HCl at 45°C

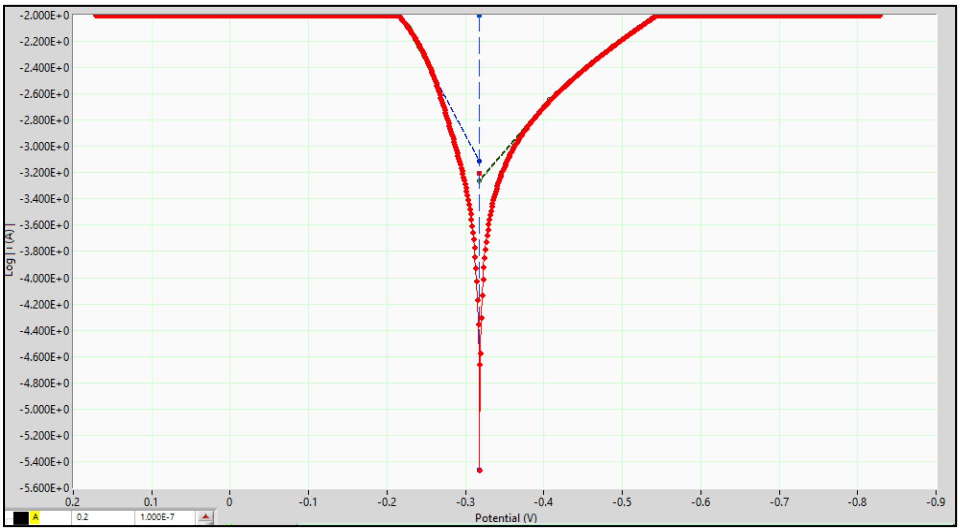


Figure 13: Tafel plot for the carbon steel alloy in presence of the optimal concentration of the complex A (50ppm) with 7 ppm of KI against of 0.1M HCl at 45°C

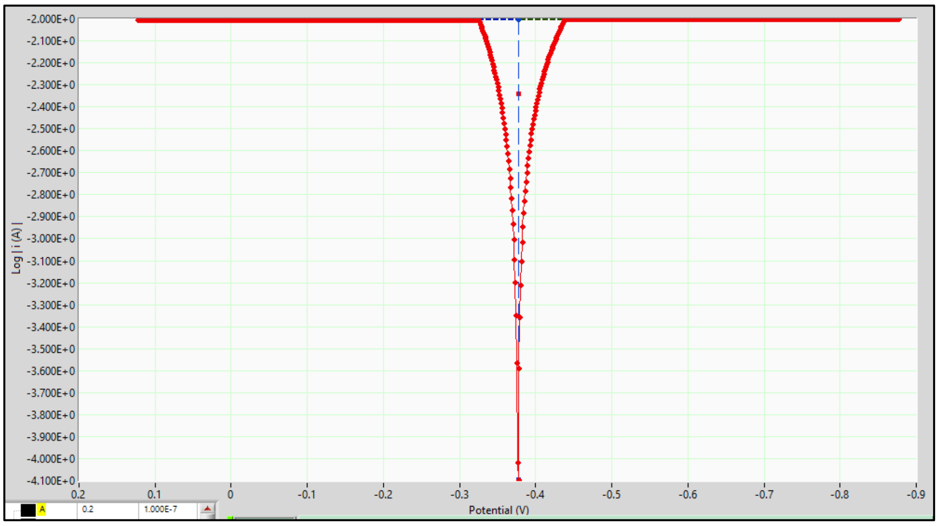


Figure 14: Tafel plot for the carbon steel alloy in presence of 0.1M HCl at 55°C

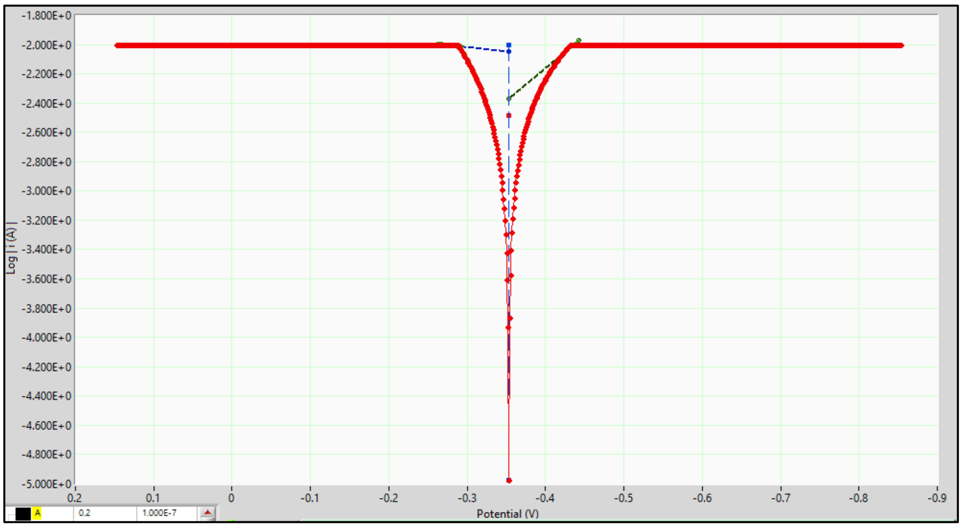


Figure 15: Tafel plot for the carbon steel alloy in presence of 7 ppm of KI against of 0.1M HCl at 55°C

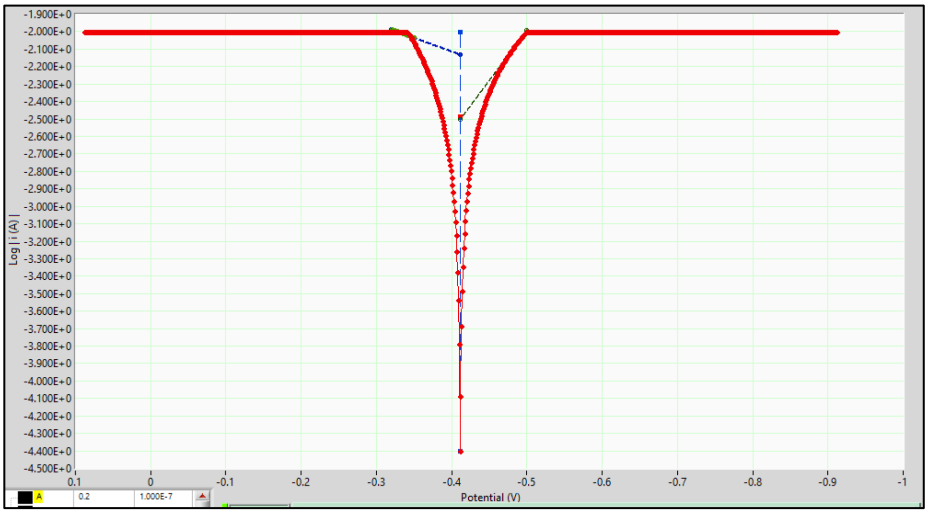


Figure 16: Tafel plot for the carbon steel alloy in presence of the optimal concentration of A (30ppm) against of 0.1M HCl at 55°C

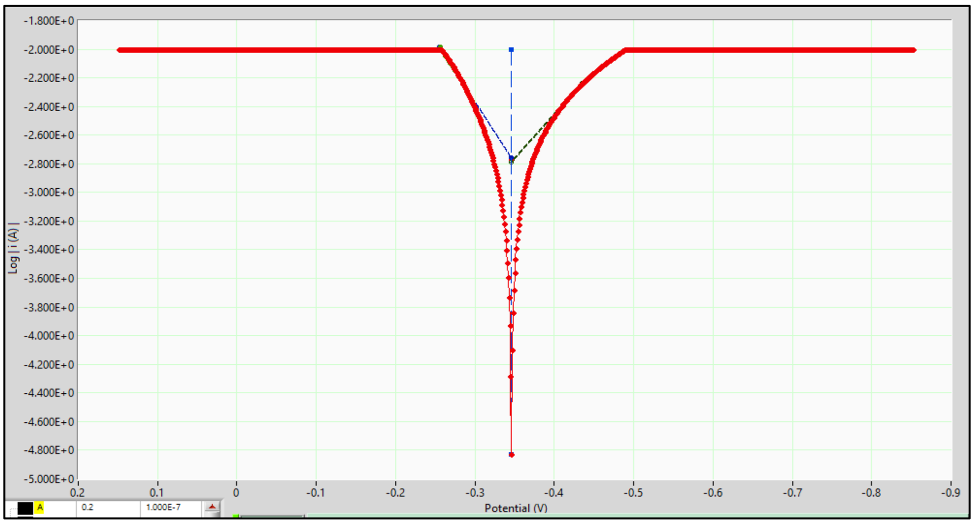


Figure 17: Tafel plot for the carbon steel alloy in presence of the optimal concentration of A (30ppm) with 7 ppm of KI against of 0.1M HCl at 55°C

The electrochemical data for the carbon steel alloy C1010 that acquired at different temperatures at range (25-55) °C are summarized in Table 2 as shown below:

Table 2: The electrochemical data that obtained by Tafel method for 0.1M of HCl and for 0.1M HCl with 7ppm of KI at different temperature

Comp.	Conc. (ppm)	Temp.(°C)	I_{corr} (μA)	CR (mpy)	E_{Corr} (V)	R_{ct} (Ω)	$β_a$ (A/V)	$β_c$ (A/V)	E %
HCl	3650	25	1375	75.44	-0.336	18.69	3.94	-6.07	-
HCl	3650	35	1841	101.04	-0.343	13.96	3.94	-6.12	-
HCl	3650	45	3088	169.44	-0.359	8.32	1.18	-5.77	-
HCl	3650	55	4567	250.6	-0.377	5.63	0	-0.04	-
KI	7	25	824.6	45.24	-0.322	31.16	10.87	-5.97	40
KI	7	35	1139	62.52	-0.319	22.56	8.36	-6.14	38
KI	7	45	2180	119.64	-0.338	11.78	6.84	-6.12	30
KI	7	55	3273	179.6	-0.353	7.85	0.52	-4.47	28

Table 3: An electrochemical data that acquired from Tafel plot of the carbon steel alloy (C1010) in presence of 10ppm of A mixed with 7 ppm of KI at different temperatures

Comp.	Temp.(°C)	I_{corr} (µA)	CR(mpy)	E_{Corr} (V)	R_{ct} (Ω)	β_a (A/V)	β_c (A/V)	E %
A_1 + KI	25	210.1	11.52	-0.224	122.4	14.11	-7.58	85
A_1 + KI	35	368.9	20.24	-0.304	69.64	12.81	-6.94	79
A_1 + KI	45	847.3	46.48	-0.319	30.32	10.19	-6.56	73
A_1 + KI	55	2065	113.32	-0.342	12.44	2.7	-6.38	55

As shown above from Table 3 as temperature increase from 25 to 55 °C, corrosion currents and corrosion rate increase as temperature increased but, the charge transfer resistance is reduced and both the values of β_a and β_c is reduced whether in absence of the inhibitors, in presence of KI alone i.e., the hydrogen evolution reaction on the cathode and the dissolution of the anode are activated [26, 30].

In same way, the effect of the temperature on the inhibition efficiency at constant concentration for each one of the inhibitor's concentrations when it mixed with 7 ppm KI, the electrochemical data that obtained are summarized at the Tables (4-7) below:

Table 4: An electrochemical data that acquired from Tafel plot of the carbon steel alloy (C1010) in presence of 20ppm of A mixed with 7 ppm of KI at different temperatures

Comp.	Temp.(°C)	I_{corr} (µA)	CR(mpy)	E_{Corr} (V)	R_{ct} (Ω)	β_a (A/V)	β_c (A/V)	E %
A_1 + KI	25	185.5	10.18	-0.318	13.85	8.26	-8.09	86
A_1 + KI	35	499.6	27.42	-0.304	51.43	10.21	-6.69	73
A_1 + KI	45	645.3	35.41	-0.313	39.82	10.41	-7.05	79
A_1 + KI	55	1673	91.84	-0.344	15.35	8.15	-6.38	64

Table 5: An electrochemical data that acquired from Tafel plot of the carbon steel alloy (C1010) in presence of 30ppm of A mixed with 7 ppm of KI at different temperatures

Comp.	Temp.(°C)	I_{corr} (µA)	CR(mpy)	E_{Corr} (V)	R_{ct} (Ω)	β_a (A/V)	β_c (A/V)	E %
A_1 + KI	25	233.9	12.84	-0.325	109.8	12.36	-7.22	83
A_1 + KI	35	374.4	20.55	-0.399	60.62	11.39	-7.04	80
A_1 + KI	45	820.9	45.04	-0.319	31.3	9.68	-6.65	74
A_1 + KI	55	1717	94.24	-0.346	14.96	8.55	-6.22	63

Table 6: An electrochemical data that acquired from Tafel plot of the carbon steel alloy (C1010) in presence of 40ppm of A mixed with 7 ppm of KI at different temperatures

Comp.	Temp.(°C)	I_{corr} (µA)	CR(mpy)	E_{Corr} (V)	R_{ct} (Ω)	β_a (A/V)	β_c (A/V)	E %
A1 + KI	25	163.7	8.98	-0.326	156.9	11.5	-7.57	88
A1 + KI	35	425.3	23.34	-0.305	60.41	9.87	-6.81	77
A1 + KI	45	918.8	50.4	-0.315	27.96	9.39	-6.94	70
A1 + KI	55	1970	108.88	-0.348	13.05	6.7	-6.16	57

Table 7: An electrochemical data that acquired from Tafel plot of the carbon steel alloy (C1010) in presence of 50ppm of A mixed with 7 ppm of KI at different temperatures

Comp.	Temp.(°C)	I_{corr} (µA)	CR(mpy)	E_{Corr} (V)	R_{ct} (Ω)	β_a (A/V)	β_c (A/V)	E %
A1 + KI	25	205.9	11.3	-0.32	124.8	11.85	-7.02	85
A1 + KI	35	414.9	22.77	-0.305	61.93	10.34	-7.1	78
A1 + KI	45	621.2	34.09	-0.318	41.36	11.3	-6.95	80
A1 + KI	55	2545	139.64	-0.352	10.1	0.24	-6.2	45

From Tables (3-7) above generally, for the inhibitor A at all concentrations (10-50) ppm as temperature increased from 25°C to 55 °C, the inhibition efficiency for the inhibitor is reduced due to the dissolving of the adsorbed layer that is coated the surface of the alloy where, the corrosion current and corrosion rate is increase but, the charge transfer resistance is reduced. On the other hand, both cathodic and anodic reaction are activated i.e., increasing in dissolution of the iron in carbon steel alloy (C1010) surface, and hydrogen evolution reactions. Hence, the inhibitor's behavior is physically adsorbed [26-27]. The cathodic and anodic reactions can be explained as below equations:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \text{ (oxidation or dissolution) (Anodic reaction)} \quad (2)$$
$$2H^{+} + 2e^{-} \rightarrow H_2 \text{ (Reduction (Hydrogen evolution) (Cathodic reaction)} \quad (3)$$

As shown from the above Tables (3-7) the behavior of KI as synergistic factor is reduced as temperature where the kinetic energy of KI molecules is increased with temperature that leads to increasing the entropy for arranging the KI with the inhibitor molecules as a protective film against the hydrochloric acid and water molecules as a corrosive molecules [32]. Thus, this case meant that the inhibitor is physically adsorbed and the corrosive molecules of HCl is entered to the surface of the carbon steel alloy (C1010) to react with Fe metal atoms i.e., dissolution of iron and hydrogen evolution reactions as in above equations 2 and 3 [33].

Furthermore, the inhibitors is activated by the synergistic effect because Cu^{2+} has the ability to back donation bonding with the organic skeleton that chelated with it due to its valance electrons with electron configuration of d^9[34]. The structure of the two inhibitors is shown below in Figure 18.

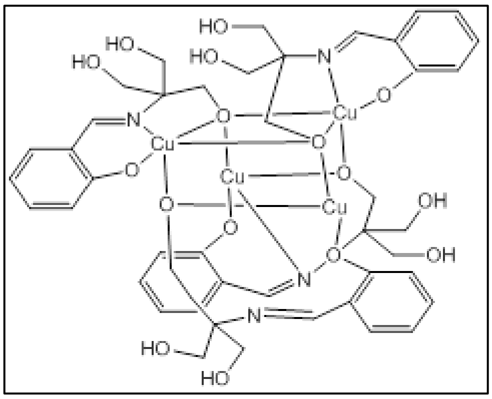


Figure 18: The structure of the inhibitor A

Where, the hydroxyl groups in phenolic rings and the aliphatic hydroxyl groups that present in A are ready to adsorbed [35] as shown above.

Adsorption isotherm study

The thermodynamic functions of adsorption like ΔG_{ads} , ΔH_{ads} and ΔS_{ads} are calculated to understand the behavior for the inhibitor on the surface of carbon steel alloy whereas, the strength of adsorption layer of the inhibitor on the surface of the alloy can be estimated according to the following equation:

$$\theta = 1 - \frac{I_{corr,inh}}{I_{corr,uninh}} \qquad (4)$$

Where θ is the surface coverage area for the alloy by the certain inhibitor, $I_{corr,inh}$ and $I_{corr,uninh}$ are the corrosion current in presence and absence of the inhibitor respectively. Hence, the equilibrium constant of the adsorption K_{ads} is calculated and the best fitted isotherm is Langmuir adsorption isotherm model where R^2 value in this model is near by the unique thus, Langmuir adsorption isotherm model [36-37] is represented by the following equation:

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

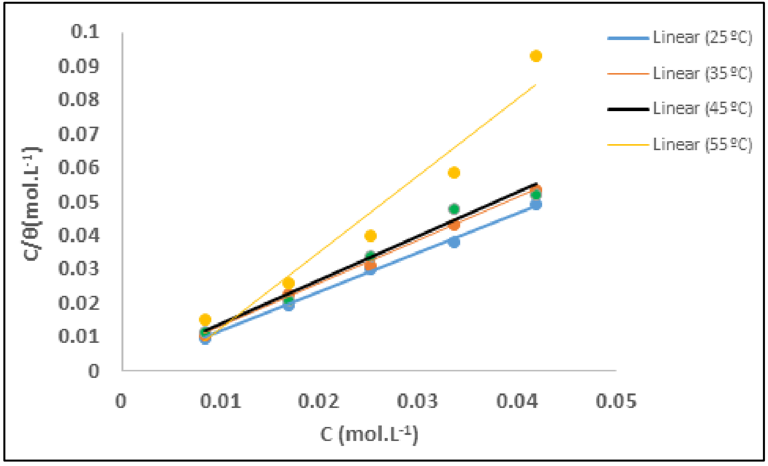


Figure 19: Calculation of K_{ads} for the inhibitor A mixed with KI at different temperatures

Figure 19 show the calculation of K_{ads} for the inhibitor that mixed with 7ppm KI at different temperatures. Then the Gibbs free energy of adsorption ΔG_{ads} is calculated according to the following equation:

$$\Delta G_{ads} = -RT\ln(55.5\,K_{ads}) \qquad (6)$$

On other hand, the enthalpy of adsorption ΔH_{ads} is calculated according to the following equation:

$$\frac{\Delta G^{\circ}_{ads}}{T} = \frac{\Delta H^{\circ}_{ads}}{T} + K \qquad (7)$$

Figure 20 explained the calculations of ΔH_{ads} and the entropy of the adsorption ΔS_{ads}:

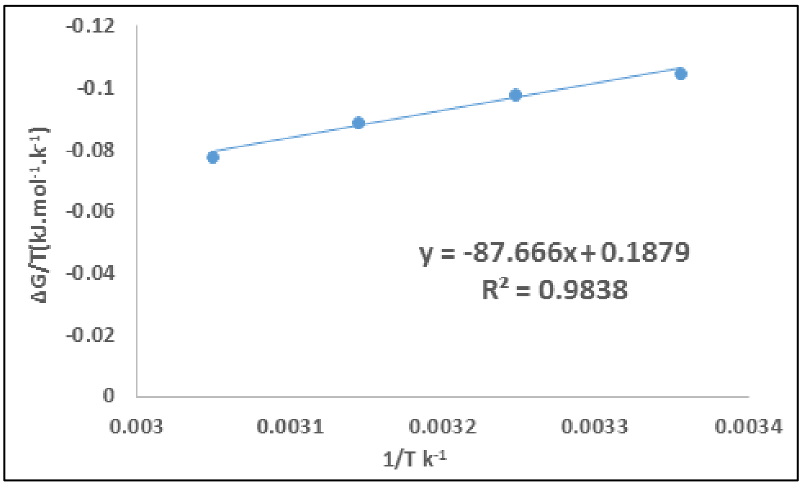


Figure 20: Calculation of the ΔH_{ads} for the inhibitor A mixed with KI

The entropy of the adsorption is calculated by the following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (8)$$

Table 8 explains the thermodynamic functions of adsorptions in the presence of the inhibitor A mixed with KI.

Table 8: Thermodynamic functions of adsorptions for the inhibitor A mixed individually with KI

Comp.	Temp. (K)	K_{ads}	R^2	ΔG_{ads} (kJ.mol^{-1})	ΔH_{ads} (kJ.mol^{-1})	R^2	ΔS_{ads} (J. mol^{-1} k^{-1})
A	298	5000	0.9978	-31.05	-87.67	0.9838	-189.99
A	308	2500	0.9975	-30.32	-87.67	0.9838	-186.2
A	318	1250	0.981	-29.47	-87.67	0.9838	-183.01
A	328	101	0.9443	-23.54	-87.67	0.9838	-195.52

From the Table 8 above R^2 is nearby to unique. For the inhibitor as temperature increased, the equilibrium constant of adsorption values are reduced meant that the adsorbed layer on the surface of alloy is reduced [30]. On the hand ΔG_{ads} and ΔH_{ads} values indicated that the adsorption reaction between the inhibitor and the surface of alloy is a spontaneous and exothermic reaction but, the spontaneously behavior is reduced as temperature increased. On the other hand, ΔS_{ads} values insist that the entropy of the adsorbed product is increased with temperature i.e., the desorption reaction is predominant as temperature increased hence, all of these data for the thermodynamic functions of adsorption are corresponding with the physically adsorbed behavior for the mentioned inhibitor [29, 31].

Kinetic study for the corrosion reaction of the carbon steel alloy in corrosive medium of 0.1M HCl

The kinetic of corrosion reaction is studied in the absence and the presence of the mixture of the inhibitor A with 7ppm of KI where, the activation energy Ea and thermodynamic functions of activations like enthalpy of activation ΔH*, Gibbs free energy if activation ΔG* and entropy of activation ΔS* are calculated. Thus, the activation of energy is calculated according to the Arrhenius equation as below:

$$\ln(i_{corr}) = \ln A - \frac{E_a}{RT} \qquad (9)$$

Where i_{corr} is the corrosion current, R is universal gas constant 8.314 J.k^{-1}.mol^{-1}, T absolute temperature and A is the frequency factor (Arrhenius's factor). Hence, the activation energy in the absence and in the presence of the inhibitor A when it mixed with 7 ppm of KI are calculated according to equation 6 above. The data are plotted as in Figure 21 below:

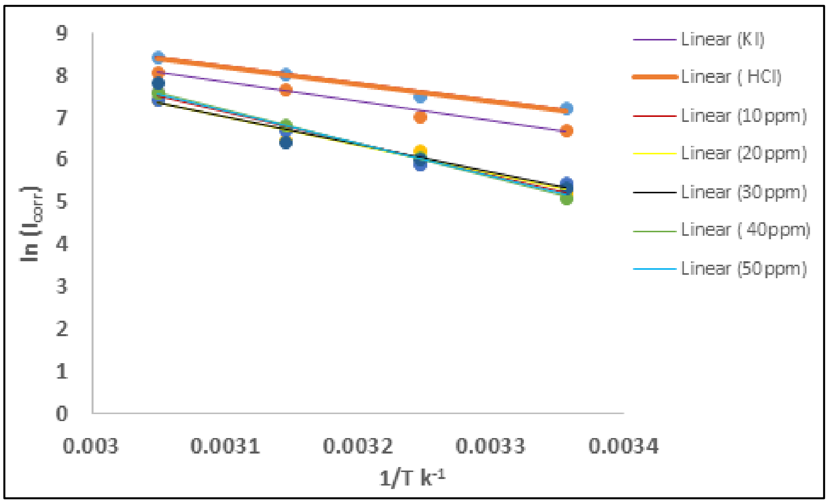


Figure 21: Calculation of the energy of activation of corrosion reaction in presence of the mixture A with 7 ppm of KI

As shown from the Figure 21 above, the energy of the activation for the corrosion reaction is reduced as the following arrange:

0.1M HCl > (inhibitor+KI)

Generally, the activation energy of the corrosion reaction in the presence of the mixture of the inhibitor A with KI is greater than in the presence of corrosive environment where, the inhibitor make the corrosion rate is reduced by inhibition the corrosive molecules of HCl to adsorbed on the surface alloy and KI has the ability to activate the inhibitor to reduce the corrosion reaction. The mentioned thermodynamic functions of activation are calculated according to the following equation by plotting ln (CR/T) against 1/T where the slope is (ΔH*/R) and the intercept is (ln(R/Nh) + ΔS*/R) [1, 4]:

$$ln\frac{CR}{T} = ln\frac{R}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad (10)$$

Where: CR is the corrosion rate in mpy, N is Avogadro's number (6.022 x 10^{23} mol^{-1}) and h is Plank's constant (6.626 x 10^{-34} J.s)

While, the Gibbs free energy of activation is calculated according the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (11)$$

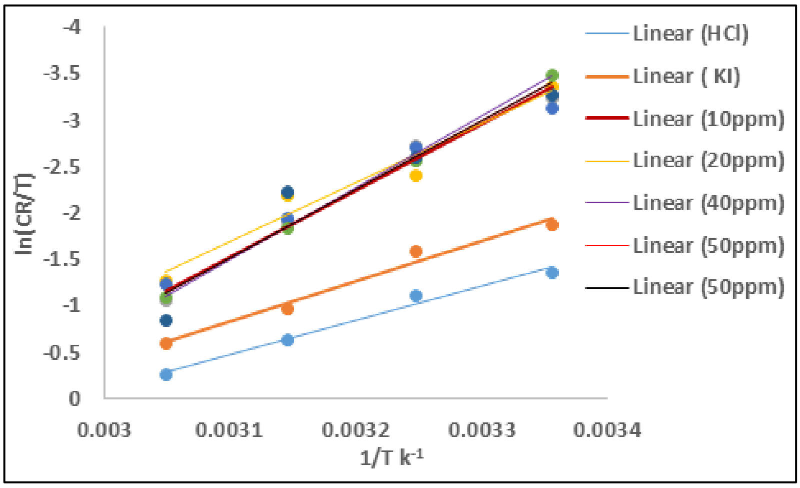


Figure 22: Calculation of the thermodynamic activation in presence of the mixture of the inhibitor A with KI

Figure 22 above explain the calculation of thermodynamic functions of activation by plotting ln (CR/T) against (1/T).
The data that acquired for the activation energy and other thermodynamic functions of activation is summarized in Table 9 below

Table 9: An activation energy and thermodynamic functions of the activation in the presence and the absence of the mixture of the inhibitor with KI

Comp.	Conc. (ppm)	E_a(kJ.mol^{-1})	ΔH* (kJ.mol^{-1})	ΔG*(kJ.mol^{-1})	ΔS*(J. mol^{-1} k^{-1})
HCl	3650	0.48	0.45	-31.16	-106.06
KI	7	0.56	0.52	-26.96	-92.2
A	10	0.9	0.86	-6.66	-25.24
A	20	0.81	0.76	-13.96	-49.39
A	30	0.79	0.77	-13.22	-46.93
A	40	0.97	0.93	-2	-9.82
A	50	0.93	0.89	-4.83	-19.19

Table 9 depicted that the corrosion rate is endothermic and it will become more endothermic in presence of the mixture of the inhibitor with KI, reducing in spontaneous and the entropy is increased in presence of the mixture above especially at 40 ppm of the inhibitor as an optimal concentration in presence of the KI with the inhibitor A these interpretations are according to the ΔH*, ΔG* and ΔS* values respectively. On the other hand, the entropy of activation in mentioned table clear that these values increased positively in the presence of inhibitor than in its absence. The increase of reveals that an increase in disordering takes place from reactant to the activated complex [27,31].

CONCLUSIONS

The inhibitor A has an efficiency 52% at 10 ppm where its efficiency is reduced as the concentration of the inhibitor is increased greater than 10 ppm compared with the other concentrations at range of (20-50) ppm at constant temperature (25 ºC) . when, the each one of the above concentration for the inhibitor A is mixed with 7 ppm of KI at 25 ºC , the efficiency of the inhibitor is increased at all its concentrations especially at 40 ppm due to the synergistic effect behavior for the KI where, the efficiency became 88%. Hence, the complex can be behaved as a good inhibitor when KI is added. The effect of the increasing the temperature from 25 ºC to 55 ºC reveals that the efficiency is reduced as the temperature increased which is corresponding with the kinetic and thermodynamic studies for the behavior of the corrosion reaction when the mixture is added compared with the absence of it whereas, the kinetic study depicted that the energy of activation is reduced in presence of the mixture, an endothermic corrosion reaction and spontaneous as temperature increased while, the adsorption and thermodynamic studies reveals that the adsorption behavior and its spontaneous is reduced as temperature increased. Furthermore , Schiff base compounds can be used to chelate the copper ions to form the complexes if it present with iron in order to reduce the corrosion hence, although the copper ions is corroded for the iron but its complexes can be used as inhibitors for iron and its alloys.

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