

CORROSION INHIBITION BEHAVIOR OF N,N'-BIS(2,4,6-TRIHIDROXYACETOPHENONE)-PROPANDIIMINE ON ST44.0 STEEL IN ALKALINE NACL SOLUTION

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Abstract: The inhibition behavior of N,N'-bis(2,4,6-trihydroxyacetophenone)-propandiimine (THAPP) as an environmentally friendly Salen Ligand on the corrosion inhibition of mild steel was studied in alkaline solution (pH=10) containing 3% NaCl. Measurements were carried out using electrochemical and surface techniques. The experimental results suggested that this compound was an effective corrosion inhibitor for mild steel and the protection efficiency was increased with the increase in inhibitor concentration. Polarization curves indicated that this organic compound was a mixed-type inhibitor. Adsorption on the mild steel surface follows the Langmuir isotherm model. Activation parameters and thermodynamic adsorption parameters of the corrosion process such as E_a , ΔH , ΔS , K_{ads} and ΔG_{ads} were calculated by the obtained corrosion currents at different temperatures.

Keywords: Corrosion, Inhibitor, adsorption isotherm, Langmuir.

1. INTRODUCTION

Carbon steel has been widely used under different conditions in various industries [1]. The corrosion processes of mild steel have been extensively studied [2] in chemical and allied industries dealing with acidic, alkaline and salt solutions [3]. Recently the corrosion behavior of mild steel in chloride contaminated alkaline solution [4-12] has received considerable attention due to its rebar corrosion problem facing by the construction industries [13, 14]. Mild steel protection in these chloride contaminated alkaline environment is due to the formation of protective iron oxide layer, magnetite [4, 15], on steel surface.

Corrosion prevention systems favor the use of corrosion inhibitors with low or zero environmental impacts. An inhibitor must move water molecules from the metal surface, interact with anodic or/and cathodic reaction sites to decrease the oxidation or/and reduction corrosion reactions, and prevent transportation of water and corrosion active species on the surface. Among three main types of inhibitors: Organic inhibitors, inorganic inhibitors and mixed material inhibitors are widely used in different solutions [16, 17].

Inhibition of organic inhibitors is due to the

interaction between inhibitor molecules and the metal surface via adsorption. The Inhibitor adsorption depends on parameters such as the surface charge and nature of the metal, the inhibitor structure, aggressive media type and the extent of aggressiveness and also on the nature of its interaction with metal surface. Furthermore, it depends on the presence of heteroatoms such as phosphorus, nitrogen, oxygen, and sulphur, aromatic rings or multiple bonds. The inhibition efficiency increases in the order $O < N < S < P$ [18-20].

These compounds decrease the corrosion rate by blocking the active surface sites. Four kinds of adsorption may occur by organic inhibitors at metal/solution interface [20-25]:

(i) electrostatic attraction between the charged molecules and charged metal, (ii) interaction between metal and uncharged electron pairs in the molecule, (iii) interaction between metal and p-electrons (iiii) both of (i) and (iii).

Different organic inhibitors such as Schiff base [16,17] have been investigated in acidic and basic environments. Nevertheless, the inhibition effect of N,N'-bis(2,4,6-trihydroxyacetophenone)-propandiimine as an environmentally friendly has not been studied in the chloride contaminated alkaline environment. This inhibitor has six

hydroxyl groups which are effective in solubility of ligand in alkaline solution and adsorption on steel surface in very low concentrations. The aim of this work is to explore the use of THAPP as an inhibitor for the corrosion of mild steel in alkaline solution (pH=10) containing 3% NaCl evaluated by Tafel polarization data. The effect of temperature and concentration on corrosion inhibition were studied. Thermodynamic parameters were calculated from experimental data of the inhibition process at different temperatures. THAPP is synthesized in simple reaction from relatively inexpensive starting-materials and has eco-friendly or low toxic properties, and harmless for environment.

2. EXPERIMENTAL DETAILS

2.1. Material Preparation

All chemicals used in present work were from reagent-grade Merck product and used as received without further purification. The THAPP Schiff base (Fig. 1) was prepared in high yield (92%) by the condensation of 2,4,6-trihydroxyacetophenone monohydrate (0.372 g, 2 mmol) with propylenediamine (0.074 g, 1 mmol) in a stirred ethanolic solution and heated to reflux for 2 h according to the described procedure [6]. The resulting precipitate was filtered off, washed with warm ethanol and diethyl ether. Identification of structure of synthesized Schiff base was performed by ¹HNMR spectroscopy and elemental analysis.

The working electrodes were prepared from mild steel specimens of the following chemical composition (wt. %): 0.21% C, 0.55% Si, 1.6% Mn, 0.04 % P, 0.04% S, 0.009% N and the remainder Fe. To prepare working electrode, steel samples (1 cm × 1 cm × 0.2 cm) were mounted in polyester in such a way that only 1 cm² of electrode was in contact with aggressive solution. The exposed area of the electrodes were mechanically abraded with 220, 600, 1000, and 2000 grades of emery paper, degreased with acetone and rinsed with distilled water before each electrochemical experiment.

All solutions were prepared from analytical grade reagents and distilled water. The aqueous medium was prepared containing 30 g/L NaCl with different concentrations of inhibitor. pH value of solutions were finally adjusted to 10 by using NaOH. The concentration range of inhibitors was varied from 1×10⁻⁶ to 7×10⁻⁵ M.

2.2. Electrochemical Measurements

Polarization experiments were performed using a Compact-stat from IVIUM Technologies controlled by a Windows-based PC running dedicated software. A three-electrode glass cell was used consisting of a platinum electrode as counter, and a saturated calomel electrode (SCE) as a reference. Before each experiment, the working electrode was immersed in the test cell at open circuit potential (EOCP) for 30 min until steady state condition was reached. The polarization curve was acquired by scanning the

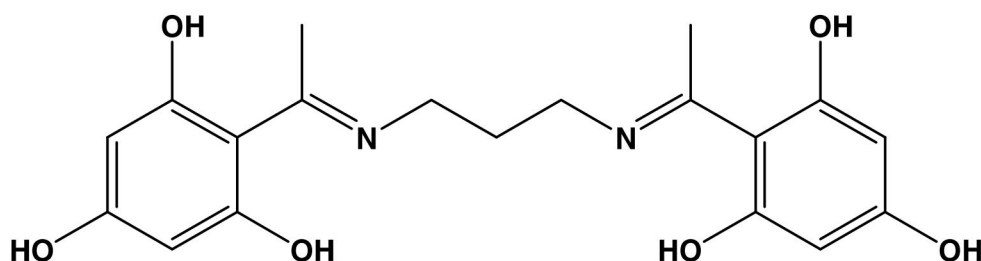


Fig. 1. Chemical structure of THAPP.

potential at constant sweep rate of 1 mV s^{-1} . The electrochemical cells were placed in a Faradaic cage to avoid electromagnetic disturbance from external sources. All tests were carried out at constant temperatures by controlling the cell temperature using a water bath. Fresh solution and fresh steel samples were used for each sweep. At least three measurements were performed to ensure the reliability and reproducibility of the data and the average values were presented. Corrosion current (I_{corr}) is calculated using the Stern–Geary equation [26, 27]:

$$= \frac{1}{\frac{b_A}{I_{\text{corr}}} + \frac{b_C}{I_{\text{corr}}}} \quad (1)$$

where b_A and b_C are the anodic and cathodic slopes respectively and R_p is the polarization resistance.

The steel specimens were grinded with emery papers, degreased in acetone, rinsed with distilled

water and dried at room temperature. Then they were immersed in the test media ($1 \times 10^{-4} \text{ M NaOH}$ solution contaminated by 3% NaCl) with and without $7 \times 10^{-5} \text{ M}$ inhibitor for 48 h. Finally the surface morphology was observed by the Scanning Electron Microscopy (VEGA\\TESCAN) at $3000\times$ magnification.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization Measurements

Fig. 2 shows the polarization curves for mild steel in the test media without and with various concentrations of inhibitor at 298 K. Table 1 shows electrochemical corrosion parameters such as corrosion potential (E_{corr} versus SCE), cathodic and anodic Tafel slopes (b_A , b_C) corrosion current density (I_{corr}), the degree of surface coverage (θ) and the inhibition efficiency ($IE\% = \theta \times 100$). These parameters were obtained by extrapolation of the Tafel lines [28]. These results reveal that the compound acts as an effective inhibitor for

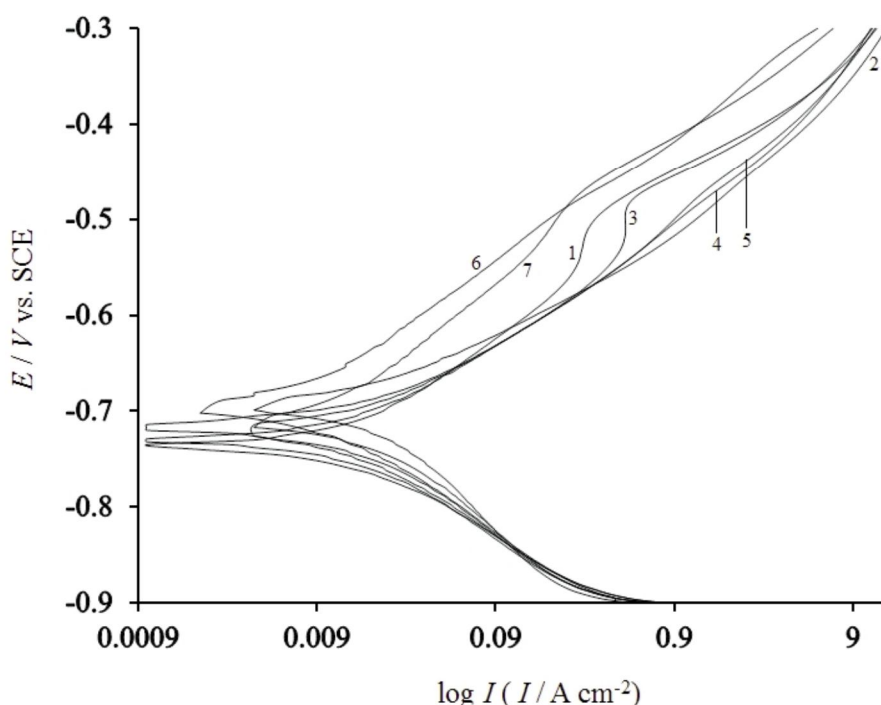


Fig. 2. Polarization curves for mild steel in alkaline 3% NaCl (pH=10) without and with various concentrations of inhibitor at 298K. 1) Blank, 2) 1×10^{-6} , 3) 3×10^{-6} , 4) 5×10^{-6} , 5) 1×10^{-5} , 6) 3×10^{-5} , 7) 7×10^{-5} .

Table 1. Potentiodynamic polarization parameters for the corrosion of mild steel in alkaline 3% NaCl (pH=10) without and with different concentrations of inhibitor at 298 K.

<i>C</i> / M	<i>E</i> _{corr} / mV	<i>I</i> _{corr} / A cm ⁻²	<i>b</i> _c / mV dec ⁻¹	<i>b</i> _a / mV dec ⁻¹	<i>R</i> _p / ohm	<i>θ</i>	<i>IE</i> %
Blank	-738.6	7	-66	84	2304	—	—
1	-694.3	6.246	-62	52	1969	0.10	10.77
3	-711.7	5.099	-48	44	1958	0.27	27.15
5	-720.6	4.582	-47	46	2212	0.34	34.54
10	-730.3	4.46	-49	50	2398	0.36	36.28
30	-696.7	4.223	-73	91	4162	0.39	39.71
70	-716.3	3.148	-47	52	3381	0.55	55.02

mild steel in alkaline NaCl solution. The degree of surface coverage for different concentrations of inhibitor is calculated using the following equation [29-31]:

$$\theta = \frac{I_{\text{corr}} - I_{\text{corr}}}{I_{\text{corr}}} \quad (2)$$

where I_{corr} and I_{corr} are the uninhibited and inhibited corrosion current densities respectively. Both the cathodic and anodic reactions are suppressed by the addition of inhibitor (Fig. 2). I_{corr} remarkably decreases, while θ increases with the inhibitor concentration. In addition corrosion potential (E_{corr}) shift has no definite trend which indicates that THAPP acts as the mixed type inhibitor, as electrode potential displacement is lower than 85 mV in any direction [32,33]. The variation in the anodic and cathodic Tafel slope with different inhibitor concentrations is relatively small. In addition, the slopes do not

display an order with the inhibitor concentration. This behavior indicates that such compound has no effect on the mechanism of either hydrogen evolution or metal dissolution and its inhibiting action occurs only by simple blocking of the available surface areas [32,33].

3.2. Effect of Temperature

To evaluate the adsorption of THAPP and activation parameters of the corrosion processes of steel, the effect of temperature was studied on inhibited solution–metal reaction (Fig. 3&4) in the temperature range of 298 K to 338 K. Table 2&3 show electrochemical corrosion parameters extracted from polarization curves at 318 K and 338 K respectively. It can be seen that I_{corr} increases by increasing temperature. The relationship between the corrosion rate and temperature is expressed by the Arrhenius equation [34]:

Table 2. Potentiodynamic polarization parameters for the corrosion of mild steel in alkaline 3% NaCl (pH=10) without and with different concentrations of inhibitor at 318 K.

<i>C</i> / M	<i>E</i> _{corr} / mV	<i>I</i> _{corr} / A cm ⁻²	<i>b</i> _c / mV dec ⁻¹	<i>b</i> _a / mV dec ⁻¹	<i>R</i> _p / ohm	<i>θ</i>	<i>IE</i> %
Blank	-816.6	29.78	-102	143	865.3	-	-
1	-803.5	19.73	-85	119	1089	0.33	33.74
3	-808.4	15.63	-74	99	1173	0.47	47.51
5	-797.5	13.35	-74	83	1272	0.55	55.17
10	-817.1	11.99	-77	85	1459	0.59	59.73
30	-823.5	10.51	-61	68	1322	0.64	64.7
70	-812.2	7.961	-56	56	1527	0.73	73.26

Table 3. Potentiodynamic polarization parameters for the corrosion of mild steel in alkaline 3% NaCl (pH=10) without and with different concentrations of inhibitor at 338 K.

C / M	E_{corr} / mV	I_{corr} / A cm^{-2}	b_c / mV dec^{-1}	b_a / mV dec^{-1}	R_p / ohm	θ	$IE\%$
Blank	-899.7	32.33	64	147	601.4	-	-
1	-929.9	23.96	70	164	877.6	0.25	25.88
3	-911.6	22.29	83	142	1024	0.31	31.05
5	-875.6	17.73	76	93	1025	0.45	45.15
10	-878.6	12.97	68	63	1094	0.59	59.88
30	-855.6	11.43	73	60	1248	0.64	64.64
70	-863	10.6	54	53	1090	0.67	67.21

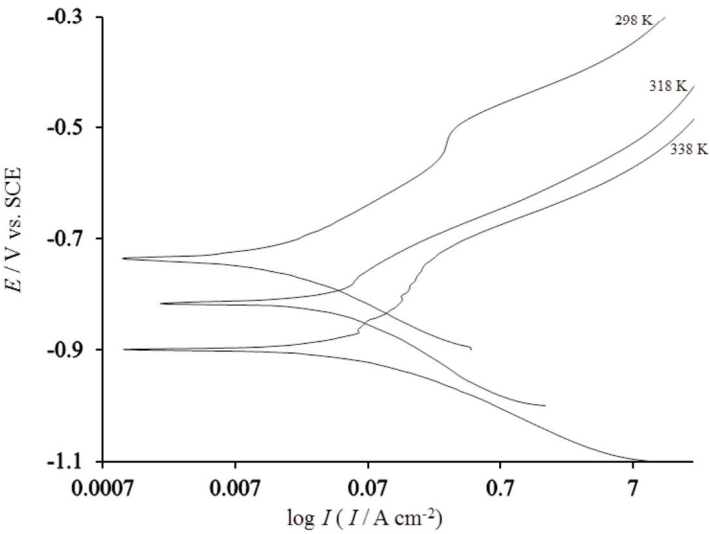


Fig. 3. Anodic and cathodic polarization curves for mild steel in alkaline 3% NaCl (pH=10) without inhibitor at different temperatures: 298 K, 318 K and 338 K.

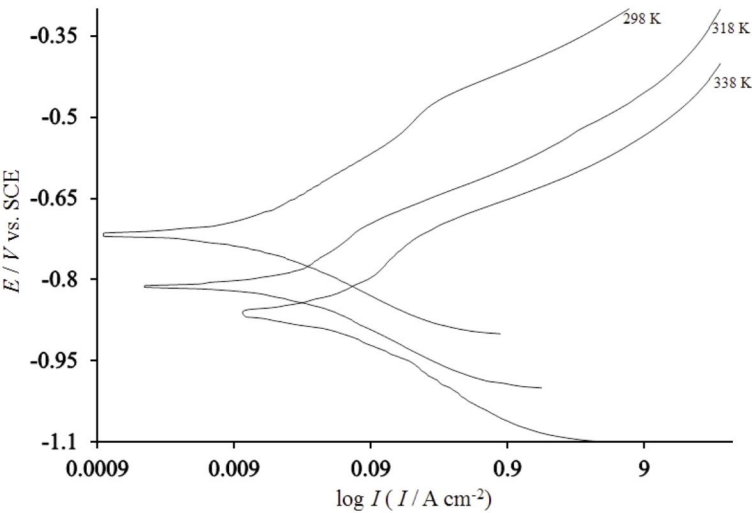


Fig. 4. Anodic and cathodic polarization curves for mild steel in alkaline 3% NaCl (pH=10) with 7×10^{-5} M of inhibitor at different temperatures: 298 K, 318 K and 338 K.

Table 4. Activation parameters of the dissolution of steel in alkaline 3% NaCl (pH=10) in the absence and in the presence of inhibitor.

C / M	E_a / kJ mol^{-1}	A / A cm^{-2}	ΔH_a / kJ mol^{-1}	ΔS_a / $\text{J mol}^{-1} \text{K}^{-1}$	$E_a - \Delta H_a = RT$ / kJ mol^{-1}
Blank	32.24	3925483.161	29.63	-127.46	2.61
1	28.25	653436.083	25.63	-142.37	2.62
3	30.89	1507555.466	28.28	-135.42	2.61
5	28.37	489921.278	25.75	-144.76	2.62
10	22.48	45161.48948	19.86	-164.59	2.62
30	20.96	22833.86454	18.34	-170.25	2.62
70	25.43	100508.7432	22.81	-157.93	2.62

= - — (3)

where A is the frequency factor, E_a is the apparent activation energy, T is the absolute temperature and R is the gas constant. The E_a value was calculated from Fig. 5 as 32.24 kJ mol^{-1} in the absence of inhibitor while in the presence of 7×10^{-5} M of inhibitor was 25.43 kJ mol^{-1} . It has been reported that the decrease in E_a with inhibitor concentration (Table 4) is typical of

chemisorption and its physisorptions is pronounced in the opposite case. Also the decrease in activation energy of corrosion at higher concentration of inhibitor is attributed to a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one [35]. Enthalpy and entropy of activation are obtained by using the formula [36]:

= — $\frac{\Delta}{}$ $\frac{-\Delta}{}$ (4)

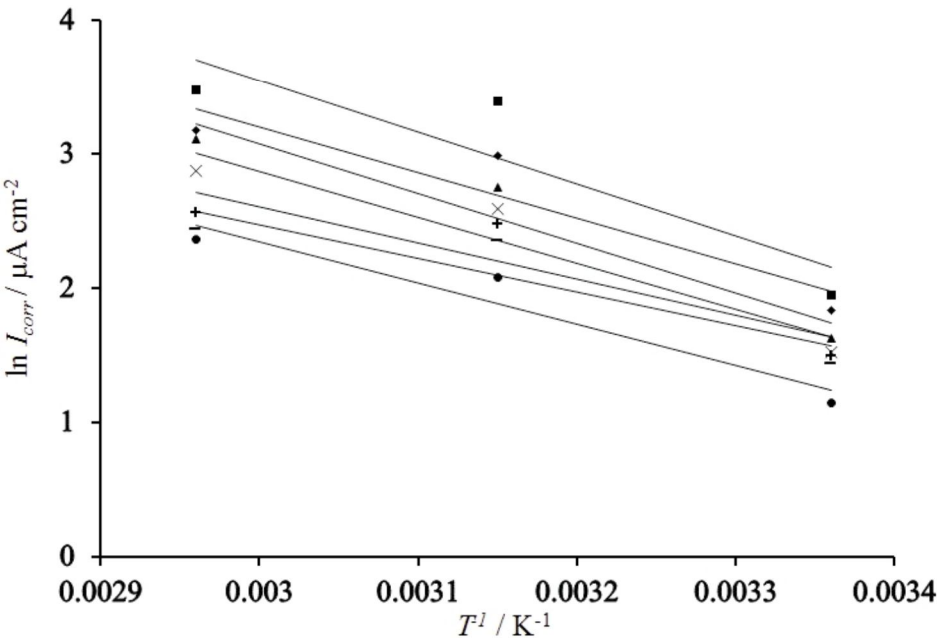


Fig. 5. Typical Arrhenius plots of $\ln I_{\text{corr}}$ vs. $1/T$ for mild steel in alkaline 3% NaCl (pH=10) at different concentrations of inhibitor: $\square$) Blank, $\diamond$) 1×10^{-6} , Δ) 3×10^{-6} , $\times$) 5×10^{-6} , $+$) 5×10^{-5} , $-$) 3×10^{-5} , $\circ$) 7×10^{-5} .

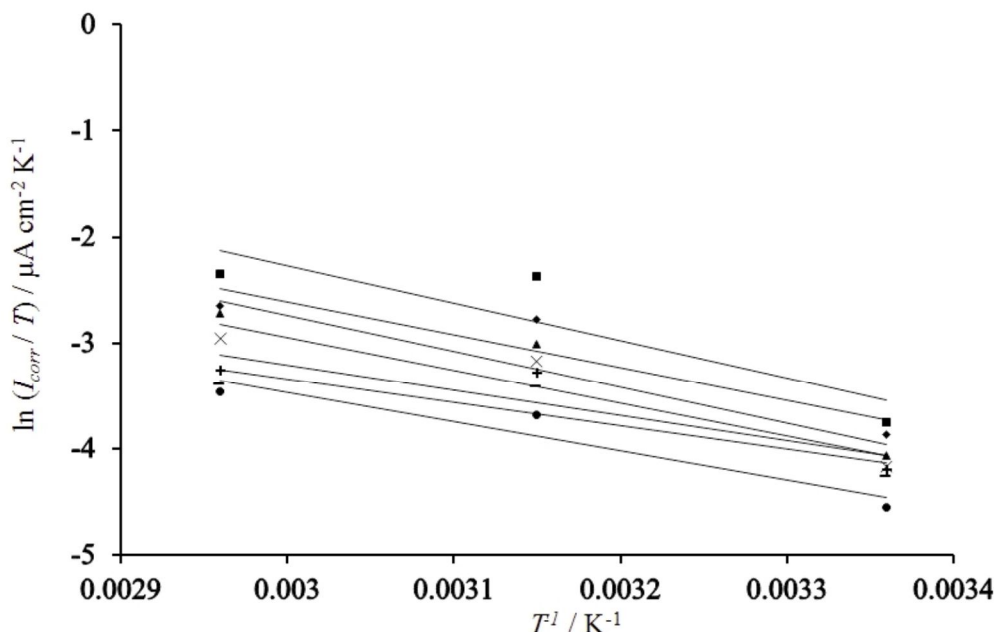


Fig. 6. Typical Arrhenius plots of $\ln(I_{\text{corr}}/T)$ vs. $1/T$ for mild steel in alkaline 3% NaCl (pH=10) at different concentrations of inhibitor: □) Blank, ◇) 1×10^{-6} , Δ) 3×10^{-6} , ×) 5×10^{-6} , +) 5×10^{-5} , -) 3×10^{-5} , ○) 7×10^{-5} .

where h is Planks constant, N is Avogadro's number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation. A plot of $\ln(I_{\text{corr}}/T)$ versus $1/T$ is shown in Fig. 6. Straight lines were obtained with a slope of $-\Delta H_a/R$ and an intercept of $(\ln R/Nh + \Delta S_a/R)$ from which the values of ΔH_a and ΔS_a were calculated in Table 4. The positive values of ΔH_a show the endothermic nature of the steel dissolution process. Also the entropy of activation increases more negatively with increasing inhibitor concentrations.

3.3. Adsorption Isotherm

It is generally agreed that corrosion inhibition is due to the adsorption of the inhibitor molecule at the metal-solution interface [37]. Adsorption isotherm importance is due to its information about the interaction between molecules and metal surface [38]. The values of surface coverage in different concentrations of the inhibitor were obtained from the polarization measurements in different temperature. The surface coverage values were used to test graphically the various adsorption isotherms

including Langmuir, Freundlich, Temkin, Frumkin, El-Awadys, Flory-Huggins and Bockris-Swinkels. To choose the isotherm, the correlation coefficient (R^2) was used and the best fit was obtained from the Langmuir isotherm ($R^2 > 0.99$), which is expressed by the following equation:

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

where C is the inhibitor concentration in the solution and K_{ads} is the equilibrium constant of the inhibitor adsorption process. Fig. 7 shows the linear relationship for the plots of C/θ versus C of inhibitor. Inspection of this figure revealed that a straight line was obtained with slopes close to unity indicated that the adsorption of THAPP obeyed Langmuir adsorption isotherm. Langmuir's adsorption assumes that each adsorbate occupy only one site on the metal surface and do not interact with the other adsorbate molecules [38]. The intercept of lines on the C/θ -axis determined the adsorption

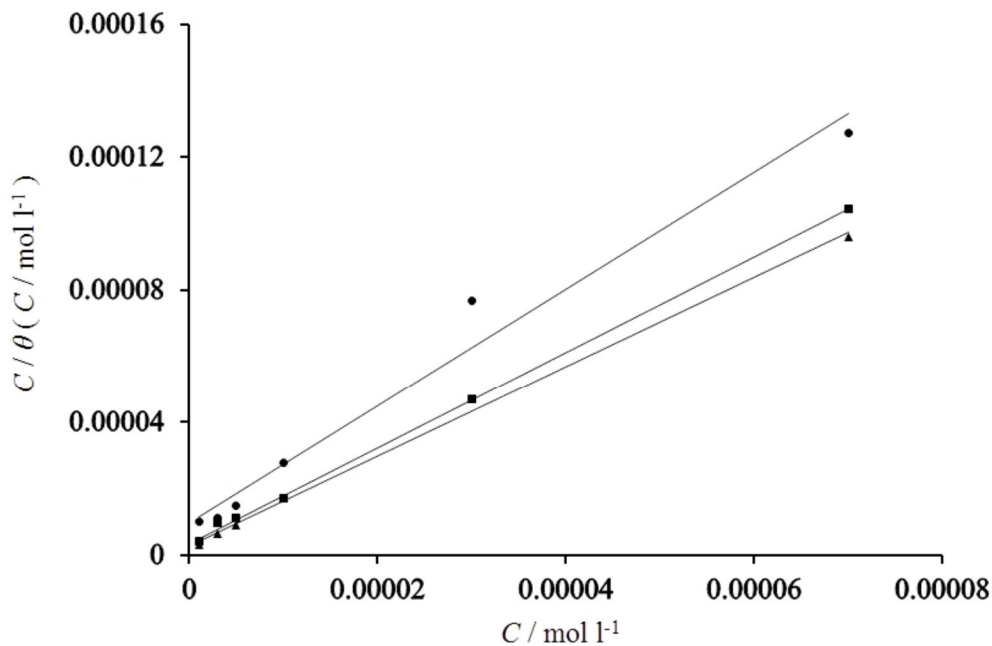


Fig. 7. Langmuir adsorption isotherm (C/θ vs. C) of inhibitor in alkaline 3% NaCl (pH=10) at different temperatures.

equilibrium constant values. The standard free energy of adsorption is related with the standard adsorption equilibrium constant of the inhibitor by the following equation:

$$\Delta G_{\text{ads}} = -RT \ln K_{\text{ads}} \quad (6)$$

The constant value of 55.5 is the concentration of water in solution expressed in molar. The enthalpy and entropy of adsorption can be deduced from the following equations [29]:

$$\Delta H_{\text{ads}} = \Delta G_{\text{ads}} - T \Delta S_{\text{ads}} \quad (7)$$

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

Enthalpy and entropy of adsorption can be obtained by plotting $\ln K_{\text{ads}}$ versus T^{-1} . Straight lines were attained with the intercept $[\Delta S_{\text{ads}}/R - \ln(55.5)]$ and the slope $-\Delta H_{\text{ads}}/R$. The calculated values of the entropy and heat of adsorption are listed in Table 5. The investigated positive value of ΔH_{ads} equal to 19.55 kJ mol⁻¹ indicates that the adsorption of THAPP on the mild steel surface is an endothermic process. An endothermic adsorption process $\Delta H_{\text{ads}} > 0$ is attributed

Table 5. Thermodynamic and equilibrium adsorption parameters for adsorption of THAPP on mild steel surface in alkaline 3% NaCl (pH=10).

$K_{\text{ads}} (-10^2) / \text{L mol}^{-1}$			$\Delta G_{\text{ads}} (-10^{-1}) / \text{kJ mol}^{-1}$			$\Delta H_{\text{ads}} / \text{kJ mol}^{-1}$	$\Delta S_{\text{ads}} / \text{J mol}^{-1} \text{K}^{-1}$
298 K	318 K	338 K	298 K	318 K	338 K		
1105	2.5105	2.5105	-38.47	-43.47	-46.21	19.55	195.80

unequivocally to chemisorption and exothermic adsorption process $\Delta H_{\text{ads}} < 0$ may involve either physisorption or chemisorption or a mixture of both the processes. Moreover the positive value of ΔS_{ads} shows that an increase in disordering takes place in going from reactants to the M_{ads} . Increasing in entropy value can be interpreted due to the more water molecules which desorbed from the metal surface by one inhibitor molecule [27]. The negative sign of the standard free energy of adsorption demonstrates the tendency of adsorption of THAPP on the metal surface and the inhibitor adsorption on the metal takes place spontaneously [39]. Values of ΔG_{ads} around -20 kJ mol^{-1} or less negative are consistent with the electrostatic interaction between organic charged molecules and the charged metal (physisorption); those around -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [40]. The values of ΔG_{ads} are more negative than -40 kJ mol^{-1} , therefore the adsorption process is chemisorption.

The chronoamperometric technique was used in order to gain more insight about the ability of the THAPP to inhibit the corrosion process of the mild steel. The electrode was polarized anodically at -0.3 V versus SCE for 600 s. The current density values associated with the electrooxidation of mild steel were recorded in the absence and in the presence inhibitor (Fig. 8). In both specimens, initially the current decreases monotonically with time. The decrease in the current density is due to the formation of corrosion products layer on the anode surface. However, in later times the current increases to reach a steady state value depending on applied potential. The increase in current is related to the dissolution of the steel and pit nucleation and pit growth. As can be seen, the current density decreases considerably in the presence of the inhibitor.

3.5. Surface Analysis

The inhibition effect of THAPP on corrosion reaction was studied by the SEM images of

Figure 7

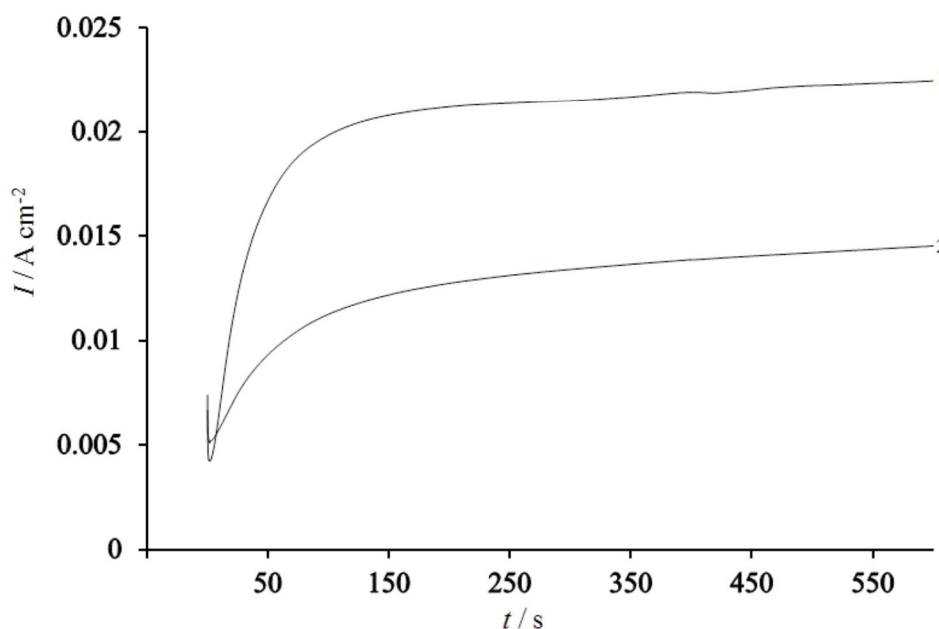


Fig. 8. Current transients of steel electrode at -0.3 V vs. SCE. (1) Blank, (2) $7 \times 10^{-5} \text{ M}$ of inhibitor.

3.4. Chronoamperometry

corroded mild steel surface in the absence and

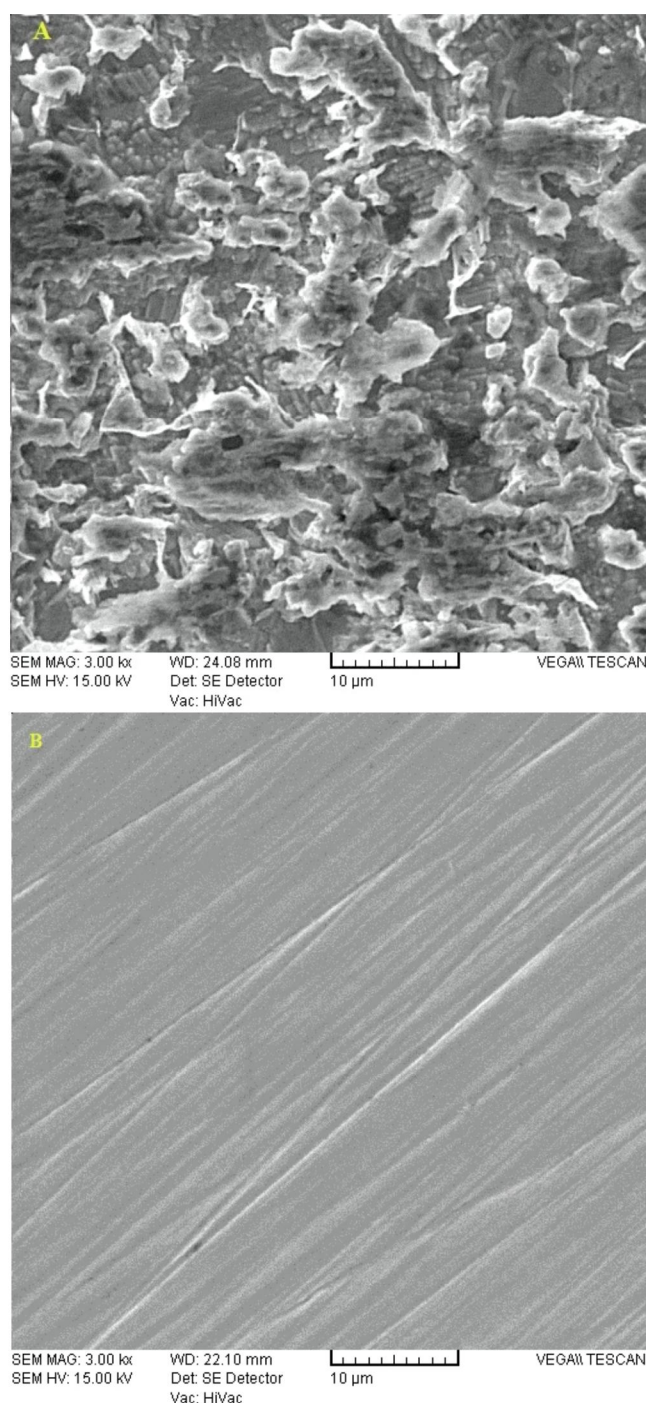


Fig. 9. SEM micrographs of the mild steel surfaces after 48 h immersion period in the blank (A) and 7×10^{-5} M of inhibitor (B) with magnification of 3000.

presence of inhibitor (Fig. 9). It can be seen that the metal surface in the blank solution (without inhibitor) corrodes uniformly (Fig. 9A) and it is strongly protected in the presence of inhibitor (Fig. 9B). These micrographs show that the

smoothness of the tested metal has remarkably improve in presence of the inhibitor in comparison with the blank one. The smoothening of the surface would have been caused by the adsorption of inhibitor molecules on the metal

surface and blocking the exposure surface from aggressive solution.

4. CONCLUSIONS

1. The THAPP acted as an effective inhibitor for mild steel corrosion in alkaline 3% NaCl solution (pH=10). Moreover because of the film formation on the metal surface, inhibition efficiency increased as the concentration of the inhibitor increased.
2. Electrochemical polarization measurements showed that the inhibitor system acted as a mixed type inhibitor. Also the adsorption of the inhibitor molecules on metal surface obeyed the Langmuir adsorption isotherm.
3. The value of ΔG_{ads} revealed that the adsorption of the inhibitor on the mild steel surface occurred through charge transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond (chemisorption).
4. Thermodynamic parameters of adsorption demonstrated that the adsorption process was spontaneous, endothermic and the molecules adsorbed on the metal surface by the process of chemisorption.
5. The SEM studies showed that the surface of sample in solution with inhibitor molecules looked smoother and more uniform with lower roughness than that in the uninhibited solution.

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