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Thiophene derivatives as corrosion inhibitors for carbon steel in hydrochloric acid solutions

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ABSTRACT

The inhibiting effect of some thiophene derivatives in 1 M HCl on the corrosion of carbon steel was studied by weight loss, potentiodynamic polarization, electrochemical frequency modulation, (EFM) and electrochemical impedance spectroscopy (EIS) techniques .The effect of temperature on the corrosion rate was investigated by the weight loss method and some thermodynamic parameters for corrosion and adsorption processes were determined and discussed. The results show that the inhibition efficiency increased with increase in inhibitor concentration and decreases with raising temperature. The adsorption of thiophene derivatives on the carbon steel surface obeys Langmuir adsorption isotherm. The obtained results indicated that the investigated compounds are physically adsorbed on the carbon steel surface. Potentiodynamic polarization studies showed that these compounds are mixed-type inhibitors and the results obtained from the different techniques are in good agreement.

Keywords: Corrosion inhibition, carbon steel, HCl, thiophene derivatives

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INTRODUCTION

Acid solutions are widely used in industry, with important fields of application including acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. Among acidic media, the hydrochloric acid used in the pickling of metals, the acidification of oil wells and the cleaning of scales is more economical, efficient and straight forward compared to other mineral acids [1].The use of inhibitors is one of the most practical methods for protection against corrosion and prevention of unexpected metal dissolution and acid consumption, especially in acid solutions.

Different organic and inorganic compounds have been studied as inhibitors to protect metals from corrosive attack. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and π-electrons [2]. Such compounds can adsorb onto the metal surface and block the active surface sites, thus reducing the corrosion rate. Although many synthetic compounds show good anticorrosive activity, most of them are highly toxic to both human beings and the environment [3], and they are often expensive and non-biodegradable. Hetero-atoms as sulfur, nitrogen and oxygen as well as aromatic rings in their structure are the major adsorption centers. Some works have studied the influence of organic compounds containing nitrogen on the corrosion resistance of steel in acidic media [4-16]. Most organic inhibitors acting by adsorption on the metal surface. To be effective, an inhibitor must be also displace water from the metals surface, to block active corrosion sites and interact with the anodic or cathodic reaction sites to retard the oxidation and/or reduction of corrosion reaction. So, the inhibition efficiency of organic compounds depends on the structure of the inhibitor, the characteristics of the environment, etc….

Several organic compounds have been evaluated as corrosion inhibitors for carbon steel in acidic media, so, the aim of this work is to study the inhibiting effect of some thiophene derivatives for the corrosion of carbon steel in 1 M HCl. The main techniques were employed chemical and electrochemical techniques. These techniques were performed in 1 M HCl without and with different concentrations of the investigated thiophene compounds.

MATERIALS AND METHODS

2.1. Materials

Rectangular specimens with dimensions 2 x 2 x 0.2 cm of carbon steel with chemical composition (weight %): C 0.20, Mn 0.35, P 0.024, Si 0.003 and Fe is the rest. For electrochemical tests, the exposed surface area of metal was 1 cm^2. Thiophene derivatives were purchased from Aldrich and used without further purifications i.e. used as received (Table 1). Hydrochloric acid (37%), ethyl alcohol and acetone were BDH grades and purchased from Algomhoria Co. (Egypt). Bidistilled water was used for preparing test solutions for all measurements.

2.2. Methods

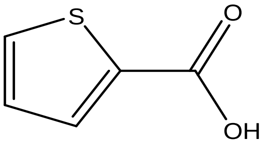
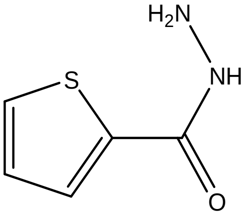
2.2.1. Weight loss measurements

Carbon steel specimens were mechanically abraded up to 1200 grades emery paper and degreased with acetone, rinsed with bidistilled water and finally dried between filter papers. After weighting accurately, the specimens were immersed in 100 ml of 1 M HCl with and without different concentrations of thiophene derivatives. After different immersion time (30, 60, 90,120,150 and180 min) the carbon steel samples were taken out, washed with bidistilled water, dried and weighted accurately. The experiments were done triplicate and the average value of the weight loss was taken. The average weight loss of the three parallel carbon steel sheets could be obtained at required temperature. The inhibition efficiency (%IE) and the degree of surface coverage (θ) of the investigated inhibitors on the corrosion of carbon steel were calculated as follows [17]:

$$\%IE = \theta \times 100 = [(W_o - W)/ W_o] \times 100 \quad (1)$$

where W_o and W are the values of the average weight loss in the absence and presence of the inhibitor, respectively.

Table 1. Molecular structures, names, molecular weights and molecular formulas of thiophene derivatives

Inh.	Structures and names	Mol. weights, Mol. formulas
TC	 2-thiophene carboxylic acid	128.15 $C_5H_4O_2S$
TCH	 2-thiophene carboxylic acid hydrazide	142.00 $C_5H_6N_2OS$

2.3.2 Potentiodynamic polarization measurements

Polarization experiments were carried out in a conventional three-electrode cell with platinum gauze as the auxiliary electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The working electrode was in the form of a square cut from C-steel sheet of equal composition embedded in epoxy resin of polytetrafluoroethylene so that the flat surface area was 1 cm^2. Prior to each measurement, the electrode surface was pretreated in the same manner as the weight loss experiments. Before measurements, the electrode was immersed in solution for 30 min. until a steady state was reached. The potential was started from - 600 to + 400 mV vs open circuit potential (E_{ocp}). All experiments were carried out in freshly prepared solutions at 25°C and results were always repeated at least three times to check the reproducibility.

2.3.3 Electrochemical impedance spectroscopy (EIS) measurements

Impedance measurements were carried out using AC signals of 5 mV peak to peak amplitude at the open circuit potential in the frequency range of 100 kHz to 0.1 Hz. All impedance data were fitted to appropriate equivalent circuit using the Gamry Echem Analyst software.

2.3.4 Electrochemical frequency modulation (EFM) measurements

EFM experiments were performed with applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5Hz was based on three arguments [18-20]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (βc and βa) and the causality factors CF-2 and CF-3[21].

All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 corrosion software, EIS300 electrochemical impedance spectroscopy software, EFM140 electrochemical frequency modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

RESULTS AND DISCUSSION

3.1. Weight-loss measurements

Weight-loss of carbon steel was determined, at various time intervals, in the absence and presence of different concentrations of thiophene derivatives (compounds: TC and TCH). The obtained weight-loss time curves are represented in Figure 1 for inhibitor TCH, the most effective one. Similar curves were obtained for other compound (not shown). The inhibition efficiency of these compounds was found to be dependent on the inhibitor concentration. The curves obtained in the presence of inhibitors fall significantly below that of free acid. In all cases, the increase in the inhibitor concentration was accompanied by a decrease in weight-loss, increase of surface coverage and an increase in the % inhibition. These results lead to the conclusion that these compounds are fairly efficient as inhibitors for carbon steel dissolution in hydrochloric acid solution. In order to get a comparative view, the variation of the % IE of the two inhibitors with their molar concentrations was calculated. The values obtained are summarized in Table 2. Careful inspection of these results showed that, at the same inhibitor concentration, the order of inhibition efficiencies is as follows: TCH > TC.

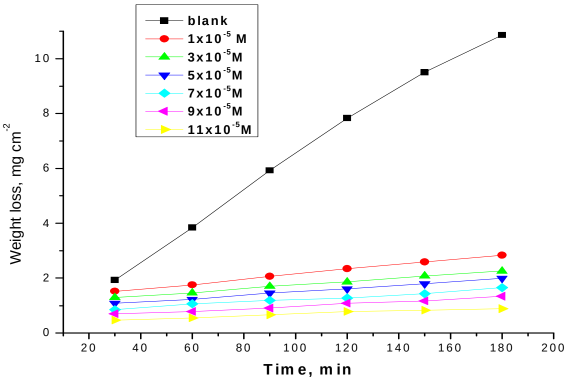


Figure 1. Weight loss-time curves for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of inhibitor TCH at 25°C

Table 2. Values of inhibition efficiencies (%IE) and surface coverage (θ) for the corrosion of carbon steel in absence and presence of different concentrations of inhibitors from weight-loss measurements at 25°C

$C_{inh.}$x10^5 M	TC		TCH	
	% IE	Θ	% IE	Θ
1	57.9	0.579	70.1	0.701
3	66.8	0.668	76.2	0.762
5	72.8	0.728	79.5	0.795
7	77.2	0.772	83.8	0.838
9	80.9	0.809	86.7	0.867
11	84.7	0.847	90.0	0.900

3.1.1. Adsorption isotherms

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system [22]. The basic information on the interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm, and the type of the inhibitors on metal is influenced by: (i) the nature and charge of the metal (ii) chemical structure of the inhibitor and (iii) the type of electrolyte [23]. The values of the degree of surface coverage (θ) were evaluated at different concentrations of the inhibitors in 1 M HCl solution. Attempts were made to fit (θ) values to various adsorption isotherms. Various adsorption isotherms were applied to fit θ values, but the best fit was found to obey Langmuir adsorption isotherm which are represented in Figure 2 for inhibitors at 25°C, Langmuir adsorption isotherm may be expressed by:

$$(\Theta/1-\Theta) = K_{ads}\, C \qquad (2)$$

where C is the concentration (mol L^{-1}) of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage, and K_{ads} is the adsorption equilibrium constant. A plot of (Θ/1-Θ) versus C should give straight lines with slope equals to K_{ads}. The experimental data give good curves fitting for the applied adsorption isotherm as the correlation coefficients (R^2) were in the range (0.991- 0.968). The values obtained are given in Table 3.

Table 3. Adsorption parameters for inhibitors in 1M HCl obtained from Langmuir adsorption isotherm at different temperatures

Comp	Temp., K	K_{ads} x10^3 M^{-1}	$-\Delta G^{\circ}_{ads}$ kJ mol^{-1}	$-\Delta H^{\circ}_{ads}$ kJ mol^{-1}	$-\Delta S^{\circ}_{ads}$ J mol^{-1} k^{-1}	R^2
TC	298	40.2	36.0	21.1	50.0	0.974
	303	34.3	36.3			0.992
	308	28.0	36.4			0.999
	313	23.6	36.8			0.995
	318	15.9	37.0			0.981
TCH	298	42.6	36.4	22.6	46.0	0.974
	303	34.6	36.5			0.985
	308	30.8	36.7			0.960
	313	28.0	37.0			0.990
	318	19.5	36.3			0.953

These results confirm the assumption that, these compounds are adsorbed on the metal surface through the lone pair of electrons of (N, S, O) atoms. The extent of inhibition is directly related to the performance of adsorption layer which is a sensitive function of the molecular structure. The equilibrium constant of adsorption K_{ads} obtained from the slope of Langmuir adsorption isotherm is related to the free energy of adsorption ΔG^{o}_{ads} as follows:

$$K_{ads} = 1/55.5 \exp(-\Delta G^{o}_{ads}/RT) \qquad (3)$$

55.5 is the molar concentration of water in the solution in M^{-1}

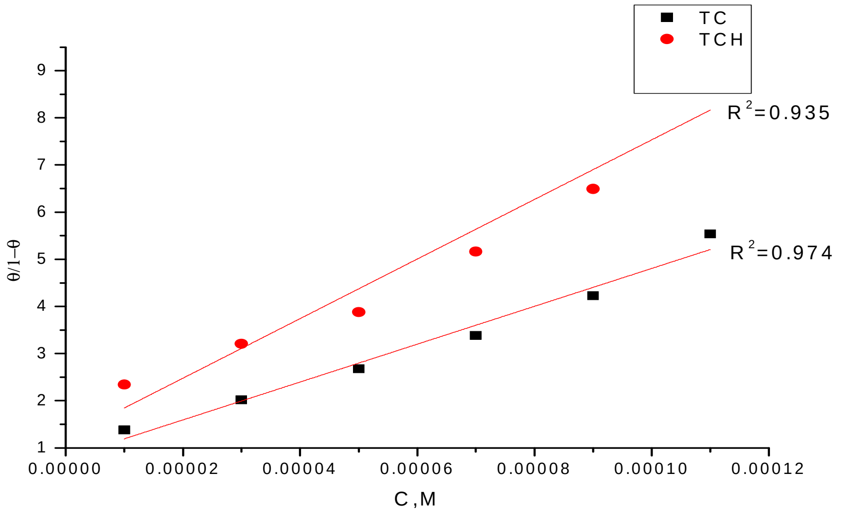


Figure 3. Curve fitting of corrosion data for carbon steel in 1M HCl in presence of different concentrations of investigated compounds to the Langmuir adsorption isotherm at 25°C

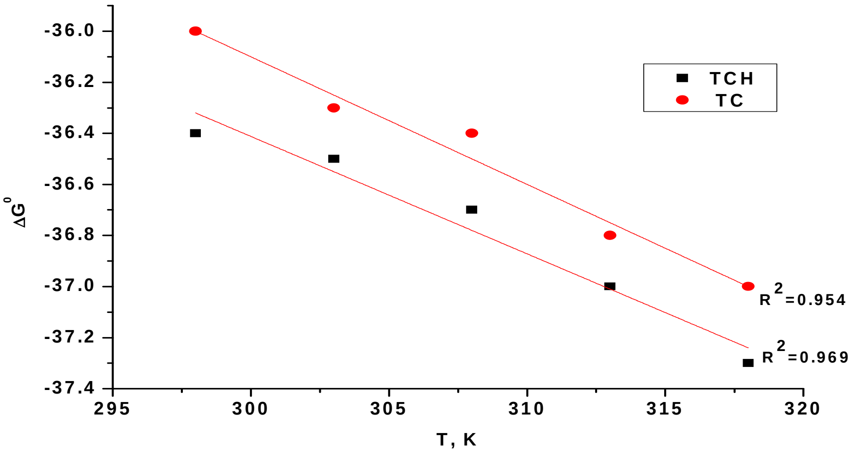


Figure 4. Variation of ΔG^o_{ads} versus T for the adsorption of inhibitors on carbon steel surface in 1 M HCl at different temperatures

Plot of (ΔG^o_{ads}) versus T (Figure 4) gave the heat of adsorption (ΔH^o_{ads}) and the standard entropy (ΔS^o_{ads}) according to the thermodynamic basic equation 4:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\,\Delta S^o_{ads} \quad (4)$$

Table (4) clearly shows a good dependence of ΔG^o_{ads} on T, indicating the good correlation among thermodynamic parameters. The negative value of ΔG^o_{ads} ensures the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. Generally, values of ΔG^o_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption);those around -40 kJ mol^{-1} or higher involves charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption)[24].The calculated ΔG^o_{ads} values are closer to -40 kJ mol^{-1} indicating that the adsorption mechanism of the inhibitors on C-steel in 1 M HCl solutions was typical of physisorption and chemisorption. The unshared electron pairs in sulphur, nitrogen as well as in oxygen may interact with d-orbitals of iron to provide a protective chemisorbed film [25]. The values of thermodynamic parameter for the adsorption of inhibitors (Table 4) can provide valuable information about the mechanism of corrosion inhibition. While an endothermic adsorption process ($\Delta H^o_{ads} > 0$) is attributed unequivocally to chemisorption [26], an exothermic adsorption process ($\Delta H^o_{ads} < 0$) may involve either physisorption or chemisorption or mixture of both processes. As, the absolute values of ΔH^o_{ads} obtained in this study was lower than (40 kJ mol^{-1}), this indicative of physisorption [27]. In the presented case, the negative values of ΔH°_{ads} indicates that these inhibitors may be adsorbed physically and chemically on C-steel surface. The ΔS^o_{ads} values in the presence of inhibitors in 1 M HCl are negative. This indicates that decrease in disorder takes places on going from reactants to the metal-adsorbed reaction complex [28].

3.1.2. Effect of temperature

The effect of temperature on the corrosion rate of carbon steel in 1 M HCl and in presence of different concentrations of inhibitors was studied in the temperature range of 298–318K using weight loss measurements. As indicated from Table 4, the rate of carbon steel dissolution increases as the temperature increases, but at lower rate than in uninhibited solutions, this indicated that the raising of temperature led to the reduction of the inhibitor adsorption and then the acceleration of dissolution process [29], which proves that the adsorption of these compounds on the surface of carbon steel occurs through physical adsorption. Similar tables was obtained for other inhibitor (not shown). Ivanov [30] considers the increase of % IE with increasing the temperature as the change in the nature of the adsorption mode; the inhibitor is being physically adsorbed at lower temperatures, while chemisorption is favored as temperature increases. Similar observations were reported by other authors [31-33].

Table 4. Values of inhibition efficiencies % IE, coverage factor (θ) and corrosion rate (C.R.) of inhibitor TCH for the corrosion of carbon steel in 1 M HCl from weight-loss measurements at different concentrations at temperatures

Conc.x 10^{-5} M	298			303			308			313			318		
	θ	**% IE**	**C.R.**	**θ**	**% IE**	**C.R.**	**θ**	**% IE**	**C.R.**	**θ**	**% IE**	**C.R.**	**θ**	**% IE**	**CR.**
1	**0.701**	**70.1**	**0.020**	**0.670**	**67.0**	**0.031**	**0.579**	**57.9**	**0.059**	**0.535**	**53.5**	**0.093**	**0.369**	**36.9**	**0.178**
3	**0.762**	**76.2**	**0.016**	**0.731**	**73.1**	**0.025**	**0.639**	**63.9**	**0.051**	**0.580**	**58.0**	**0.084**	**0.437**	**43.7**	**0.159**
5	**0.795**	**79.5**	**0.013**	**0.786**	**78.6**	**0.020**	**0.674**	**67.4**	**0.046**	**0.634**	**63.4**	**0.073**	**0.498**	**49.8**	**0.142**
7	**0.838**	**83.8**	**0.011**	**0.811**	**81.1**	**0.018**	**0.741**	**74.1**	**0.036**	**0.713**	**71.3**	**0.058**	**0.559**	**55.9**	**0.125**
9	**0.867**	**86.7**	**0.009**	**0.834**	**83.4**	**0.016**	**0.776**	**77.6**	**0.031**	**0.742**	**74.2**	**0.052**	**0.607**	**60.7**	**0.111**
11	**0.900**	**90.0**	**0.007**	**0.886**	**88.6**	**0.011**	**0.825**	**82.5**	**0.025**	**0.809**	**80.9**	**0.038**	**0.676**	**67.6**	**0.092**

3.1.3. Kinetic –thermodynamic corrosion parameter

The activation parameters for the corrosion process were calculated from Arrhenius-type plot according to equation 5:

$$k_{corr} = A \exp -E^*_a/RT \qquad (5)$$

where E^*_a is the apparent activation corrosion energy, R is the universal gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential constant. Values of apparent activation energy of corrosion (E^*_a) for carbon steel in 1 M HCl without and with various concentrations of compound TCH are shown in Table 5. These values were determined from the slope of log (k_{corr}) versus 1/T plots (Figure 5). The results of Table 5 showed that the value of (E^*_a) for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of carbon steel is slow in the presence of the inhibitors. It is known from Arrhenius equation that the higher (E^*_a) values lead to the lower corrosion rate, this is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion [34]. Schmid and Huang [35] found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but the reaction rate on the covered area is substantially less than on the uncovered area similar to the present study. The alternative formulation of transition state equation is shown in Eq. 6:

$$k_{corr} = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (6)$$

where k_{corr} is the rate of metal dissolution, h is Planck's constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Figure 7 shows a plot of (log k_{corr}/T) against (1/T) in the case of inhibitor TCH in 1 M HCl. Similar behavior is observed in the case of inhibitor TC (not shown). Straight lines are obtained with a slopes equal to (ΔH^* /2.303R) and intercepts are [log (R/Nh + ΔS^*/2.303R)] are calculated (Table 5).

Table 5. Kinetic activation parameters for carbon steel in 1 M HCl in the absence and presence of different concentrations of investigated inhibitors

Comp	Conc., x 10^5 M	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J $mol^{-1}K^{-1}$
Blank	0.0	24.9	53.6	90.2
TC	1	30.1	69.3	44.1
	3	31.0	71.0	38.5
	5	32.1	71.5	36.3
	7	32.2	73.7	32.7
	9	34.8	75.8	27.1
	11	34.9	79.9	15.1
TCH	1	33.1	81.1	5.5
	3	35.3	86.3	10.1
	5	36.2	88.2	15.1
	7	38.9	89.0	15.3
	9	39.5	90.5	19.1
	11	40.6	91.6	20.6

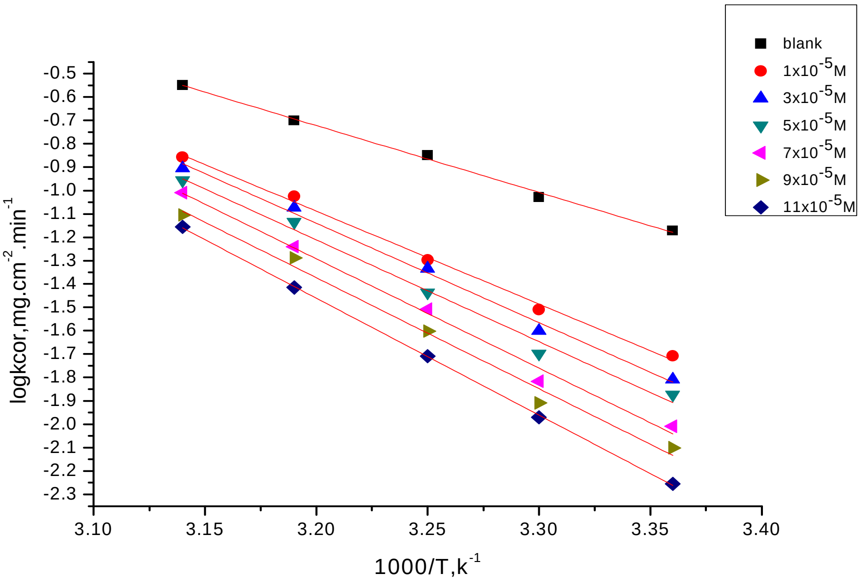


Figure 6. Log k_{corr} vs. 1/T curves for Arrhenius plots for carbon steel corrosion rates ($k_{corr.}$) after 120 minutes of immersion in 1M HCl in the absence and presence of various concentrations of inhibitor TCH

The positive signs of the enthalpies (ΔH^*) reflect the endothermic nature of the steel dissolution process. The entropy of activation in presence and absence of the inhibitor was large and negative. This implies that the activated complex in the rate determining step represents association rather than dissociation, indicating that a decrease in disorder takes place, going from reactant to the activated complex [36].

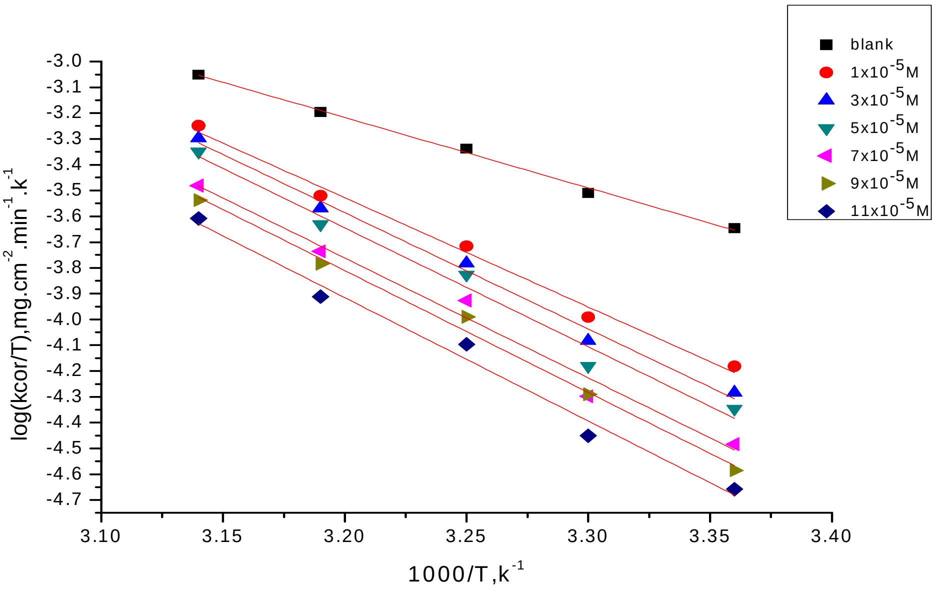


Figure 7. Log (k_{corr}/T) vs. (1/T) curves for Arrhenius plots for carbon steel corrosion rates ($k_{corr.}$) after120 minutes of immersion in 1 M HCl in the absence and presence of various concentrations of inhibitor TCH

3.1. Electrochemical frequency modulation (EFM) measurements

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current values without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [37].The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Figure 8 shows the EFM Intermodulation spectra (current vs frequency) of carbon steel in 1 M HCl solution with and without 11 x 10^{-6} M concentrations of compound TCH. Similar curves were obtained for other concentrations and compound TC (not shown). The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 200 μA, are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 nA). The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the “activation” model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode [38].The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF-2 and CF-3. These electrochemical parameters were listed in Table 6. The data presented obviously show that, the addition of any one of tested compounds at a given concentration to the acidic solution decreases the corrosion current density, indicating that these compounds inhibit the corrosion of carbon steel in 1 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality. The inhibition efficiencies % IE_{EFM} increase by increasing the inhibitor concentrations and was calculated as from Eq. 8:

$$\%IE_{EFM} = [1-(i_{corr}/i^{o}_{corr})] \times 100 \qquad (8)$$

where i^{o}_{corr} and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively. The inhibition sufficiency obtained from this method is in the order: TCH > TC

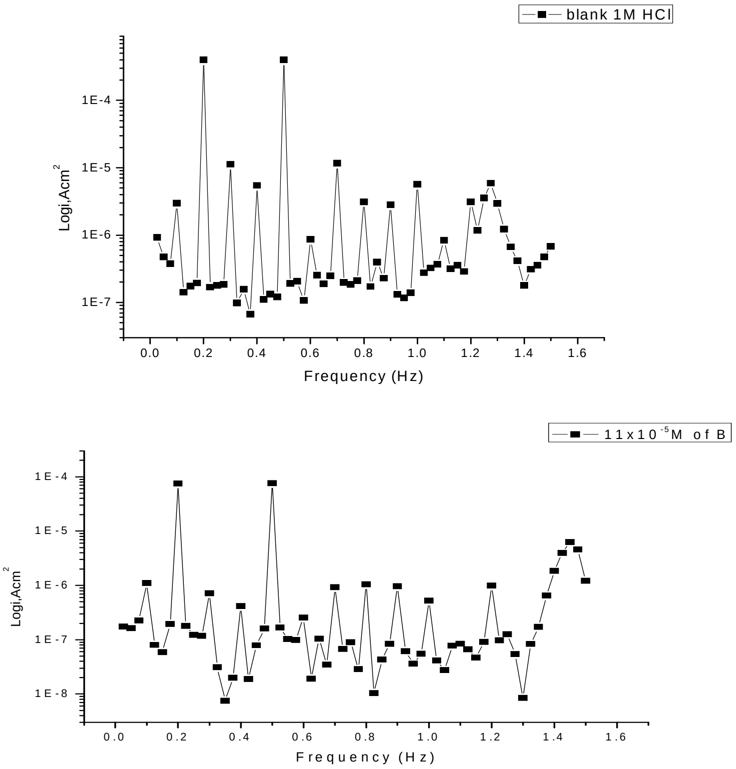


Figure 8. EFM spectra for carbon steel in 1 M HCl in the absence and presence of different concentrations of compound TCH

Table 6. Electrochemical kinetic parameters obtained by EFM technique for carbon steel in the absence and presence of various concentrations of inhibitors in 1M HCl at 25°C

Comp	Conc., x 10^{-5} M	i_{corr}, µAcm^{-2}	β_c, mVdec^{-1}	β_a, mVdec^{-1}	CF-2	CF-3	C.R , mpy	θ	% IE
Blank	0.0	831.2	154	121	2.06	3.89	380.0	-	-
TC	1	350.3	160	130	1.85	1.71	160.1	0.579 6666666666666666666666666666666666666	57.9
	3	346.1	144	114	1.89	3.72	158.1	0.584	58.4
	5	343.4	129	103	2.15	2.92	156.9	0.587	58.7
	7	298.9	137	128	1.73	3.25	136.6	0.640	64.0
	9	212.4	113	109	2.34	3.71	97.05	0.744	74.4
	11	185.0	136	123	1.34	1.01	84.54	0.777	77.7
TCH	1	342.0	71	64	1.22	1.16	156.3	0.589	58.9
	3	337.0	73	55	1.32	1.32	154.0	0.595	59.5
	5	322.0	43	36	1.60	1.92	147.1	0.613	61.3
	7	229.2	25	23	1.79	2.98	104.7	0.724	72.4
	9	165.4	93	90	1.69	3.34	75.6	0.801	80.1
	11	113.9	102	95	1.75	1.41	52.1	0.863	86.3

3.2 Electrochemical impedance spectroscopy (EIS) measurements

It is powerful technique for studying the corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from impedance diagrams [39-43]. Figure 9 shows the Nyquist plots obtained at open-circuit potential both in the absence and presence of increasing concentrations of investigated TCH at 25°C. The increase in the size of the capacitive loop with the addition of investigated compounds shows that a barrier gradually forms on the carbon steel surface. The increase in the capacitive loop size enhances at a fixed inhibitor concentration, following the order: TCH > TC, confirming the highest inhibitive influence of compound TCH. The Nyquist plots do not yield perfect semicircles as expected from the theory of EIS. The deviation from ideal semicircle was generally attributed to the frequency dispersion [44] as well as to the inhomogenities of the surface.

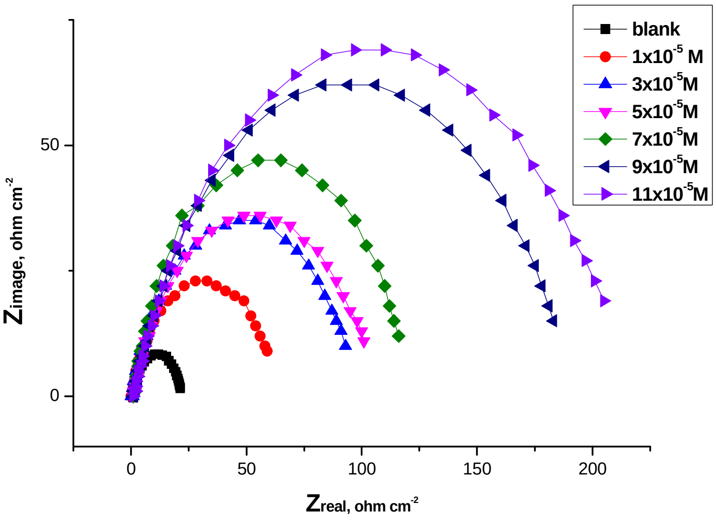


Figure 9. The Nyquist plots for the corrosion of carbon steel in 1M HCl in the absence and presence of different concentrations of inhibitor TCH at 25° C

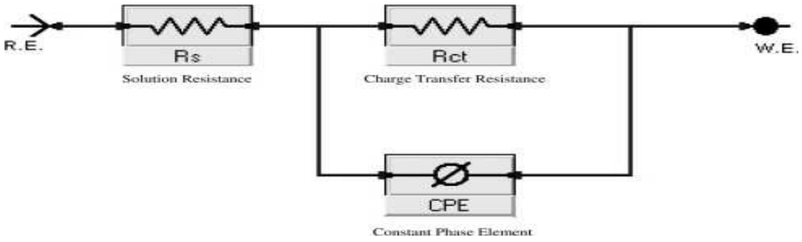


Figure 10. Equivalent circuit model used to fit experimental EIS

EIS spectra of the investigated compounds were analyzed using the equivalent circuit, Figure 10, which represents a single charge transfer reaction and fits well with our experimental results. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [45].The double layer capacitance, C_{dl}, for a circuit including a CPE parameter (Y_0 and n) were calculated from Eq. 9 [46] :

$$C_{dl} = Y_0\omega^{n-1} / \sin [n (\pi/2)] \qquad (9)$$

whereY_0 is the magnitude of the CPE, $\omega = 2\pi f_{max}$, f_{max} is the frequency at which the imaginary component of the impedance is maximal and the factor n is an adjustable parameter that usually lies between 0.5 and 1.0. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charged-transfer controlled [47,48] .The general shape of the curves is very similar for all samples (in presence or absence of inhibitors at different immersion times) indicating that no change in the corrosion mechanism [49] From the impedance data (Table 7), we concluded that the value of R_{ct} increases with increasing the concentration of the inhibitors and this indicates an increase in % IE_{EIS}, which in concord with the EFM results obtained. In fact the presence of inhibitors enhances the value of R_{ct} in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of CPE follows the order similar to that obtained for i_{corr} in this study. The decrease in CPE/C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggesting that organic derivatives inhibit the iron corrosion by adsorption at metal/acid [50] .The inhibition efficiency was calculated from the charge transfer resistance data from equation 10:

$$\% IE_{EIS} = [1 -(R°_{ct}/ R_{ct})] \times 100 \qquad (10)$$

where R^o_{ct} and R_{ct} are the charge-transfer resistance values without and with inhibitor respectively.

Table 7. Electrochemical kinetic parameters obtained from EIS technique for carbon steel in 1M HCl in the absence and presence of different concentrations of investigated compounds

Comp	Conc., x 10^{-5}M	R_S, Ωcm^2	Y^o, $\mu\Omega^{-1} s^n cm^{-2}$	n	R_{ct}, $\Omega\ cm^2$	C_{dl}, $\mu F cm^{-2}$	θ	%IE
Blank	0.0	0.811	1250.8	0.844	21.04	637.2	---	---
TC	1	1.082	1198.0	0.758	77.48	554.3	0.728	72.8
	3	1.060	1052.0	0.776	84.32	523.6	0.750	75.0
	5	1.013	968.9	0.778	95.37	491.6	0.780	78.0
	7	1.102	836.5	0.783	103.80	424.8	0.797	79.7
	9	1.145	730.9	0.773	123.70	361.9	0.830	83.0
	11	1.323	611.0	0.781	170.10	323.6	0.876	87.6
TCH	1	0.807	399.0	0.832	83.0	200.0	0.747	74.7
	3	0.795	348.8	0.819	95.34	164.3	0.779	77.9
	5	1.422	320.0	0.788	105.40	128.7	0.801	80.1
	7	1.725	210.4	0.861	115.10	115.4	0.817	81.7
	9	1.459	180.6	0.856	142.50	97.5	0.852	85.2
	11	1.406	175.8	0.755	206.50	60.0	0.898	89.8

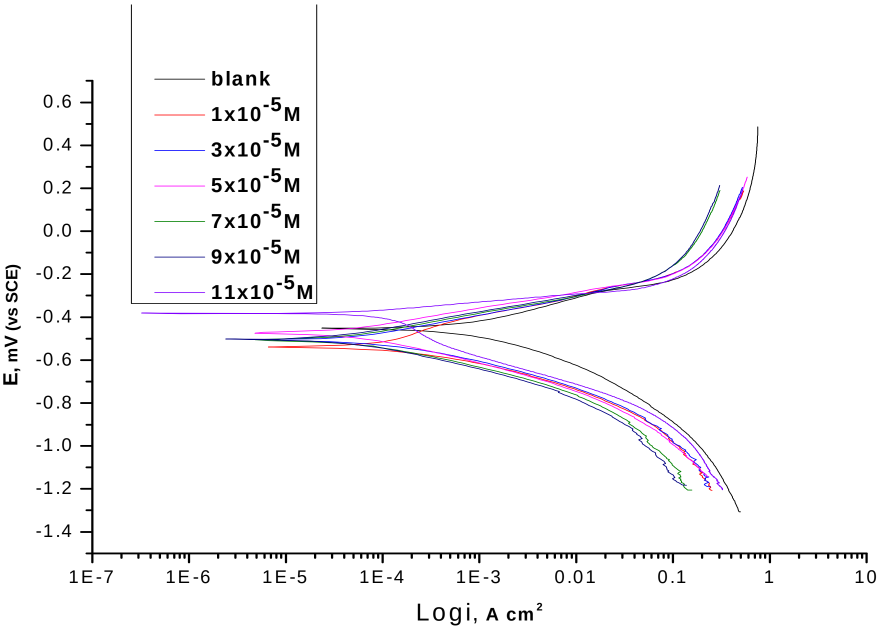


Figure 11. Potentiodynamic polarization curves for the dissolution of C- steel in 1 M HCl in the absence and presence of different concentrations of compound TCH at 25°C

3.3 Potentiodynamic polarization measurements

Figure (11) shows the potentiodynamic polarization curves of carbon steel dissolution in 1 M HCl in the absence and presence of different concentrations of inhibitor TCH at 25°C. Similar curves were obtained for other inhibitor (not shown). The numerical values of the variation of the corrosion current density (i_{corr}), the corrosion potential (E_{corr}), Tafel slopes (β_a and β_c),), the degree of surface coverage (Θ) and the inhibition efficiency were recorded in Table 8. The inhibition efficiency and degree of surface coverage were calculated using equation 11:

$$\%IE_p = \theta \times 100 = [(i^o_{corr} - i_{corr}) / i^o_{corr}] \times 100 \qquad (11)$$

where i^o_{corr} and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively. The results of Table 8 indicate that:

1. The cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of thiophene derivatives increased both the cathodic and anodic overvoltage and inhibits both the hydrogen evolution and the anodic dissolution processes i.e. mixed type inhibitors.
2. The corrosion current density ($i_{corr.}$) decreases with increasing the concentration of the thiophene derivatives which indicates that these compounds act as inhibitors, and the degree of inhibition depends on the concentration and type of inhibitors present.
3. The slopes of anodic and cathodic Tafel lines (β_a and β_c)), were slightly changed on increasing the concentration of the tested compounds. This indicates that these inhibitors act as mixed-type inhibitors. Tafel lines are parallel, which indicates that there is no change of the mechanism of inhibition in the presence and absence of inhibitors.
4. The orders of inhibition efficiency of inhibitors at different concentrations as given by polarization measurements are in good agreement with those obtained from weight-loss measurement, FEM and EIS techniques

Table 8. Corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_c,β_a), and degree of surface coverage (θ), and inhibition efficiency (% IE_p) of carbon steel in 1M HCl at 25°C for investigated compounds

Comp	Conc.,x 10^{-5} M	-E_{corr}, mVvs SCE	$i_{corr,}$ µA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	C.R., mpy	ϴ	% IE
blank	0	453	972	200	129	444.3	-----	------
TC	1	547	190	102	884	86.8	0.805	80.5
	3	584	141	89	617	64.4	0.855	85.5
	5	542	121	101	152	55.3	0.876	87.6
	7	536	117	128	123	53.4	0.880	88.0
	9	538	108	114	136	49.5	0.889	88.9
	11	531	86.1	105	145	39.3	0.911	91.1
TCH	1	538	99.2	109	130	45.3	0.898	89.8
	3	506	90.4	122	104	41.3	0.907	90.7
	5	473	55	130	85	25.1	0.943	94.3
	7	506	51.7	119	96	23.4	0.947	94.7
	9	503	46.3	116	94	21.2	0.952	95.2
	11	382	22.1	124	33	10.1	0.977	97.7

3.4. Mechanism of corrosion inhibition

Inhibition efficiency of carbon steel corrosion in 1 M HCl solution by thiophene derivatives using the above techniques was found to depend on the number of adsorption active sites in the molecule and their charge density, molecular size and stability of these derivatives in acidic solutions [51]. Generally, the heterogeneous organic compounds having higher basicity and electron density on the hetero atoms such as N, O, and S, have tendency to resist corrosion. Nitrogen and oxygen are the active centers for the process of adsorption on the metal surface. These compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion attack. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present, the p orbital character of free electrons and the electron density around nitrogen and oxygen atoms [52]. The compounds containing both nitrogen and sulfur can provide efficient inhibition, compared with compounds containing only nitrogen or sulfur [53]. The cationic organic inhibitors in the presence of the chloride ions show synergistic effect in the inhibition of corrosion, these compounds are not good inhibitors in plain sulfuric acid media as a result of strong adsorption of sulfate ions on the metal surface [54]. The inhibition effect of these compounds is attributed to the adsorption of the inhibitor molecules on the metal surface. The adsorption is assumed to take place mainly through the nitrogen, oxygen and sulphur atoms in thiophene derivatives (active centers). The order of inhibition efficiency of investigated compounds is as follows: TCH > TC. From the above sequence of % IE, it is clear that the compound TCH is more efficient inhibitor for corrosion of tin in 1 M HCl solution. This is most probably due to, the presence of 2N, O, S adsorption centers. Compound TC comes after compound TCH in %IE, because it contains 2O, S atoms as adsorption centers.

CONCLUSION

From the results of the study the following may be concluded:

All the investigated compounds are good corrosion inhibitors for carbon steel in 1 M HCl solution. The effectiveness of these inhibitors depends on their structures. The variation in inhibitive efficiency depends on the type and the nature of the substituent present in the inhibitor molecule. Reasonably good agreement was observed between the values obtained by the weight loss and electrochemical measurements. The order of % IE of these investigated compounds is in the following order: B > A. Results obtained from potentiodynamic polarization indicated that the investigated compounds are mixed-type inhibitors. Percentage inhibition efficiency of thiophene derivatives was temperature dependent and its addition led to an increase of the activation energy. The results of EIS revealed that an increase in the charge transfer resistance and a decrease in double layer capacitance when the inhibitor is added and hence an increase in % IE. This is attributed to increase of the thickness of the electrical double layer. The adsorption of thiophene derivatives onto steel surface follows the Langmuir adsorption isotherm model (physisorption). EFM can be used as a rapid and nondestructive technique for corrosion measurements without prior knowledge of Tafel slopes.

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