

ROLE OF SOME THIOUREA DERIVATIVES AS CORROSION INHIBITORS FOR CARBON STEEL IN ACIDIC MEDIUM

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ABSTRACT

The inhibiting action of some thiourea derivatives as corrosion inhibitors for C- steel in 2 M HCl have been studied using potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques. Polarization studies were carried out at room temperature, and showed that all the compounds studied are mixed type inhibitors. The effect of temperature on corrosion inhibition has been studied and the thermodynamic activation and adsorption parameters were calculated to elaborate the mechanism of corrosion inhibition. Electrochemical impedance was used to investigate the mechanism of corrosion inhibition. The presence of these compounds in the solution decreases the double layer capacitance and increases the charge transfer resistance. The adsorption of these compounds on C-steel surface was found to obey Temkin's adsorption isotherm. The synergistic effect brought about by combination of the inhibitors and KSCN, KI and KBr was examined and explained. The mechanism of inhibition process was discussed.

Key words: thiourea derivatives; corrosion inhibition; C-steel; HCl.

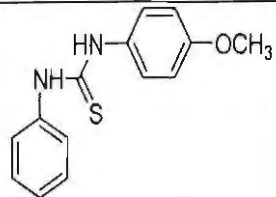
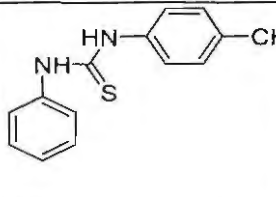
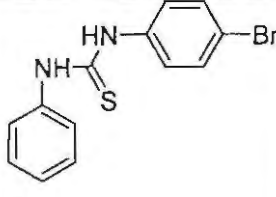
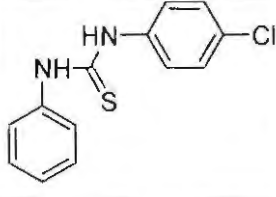
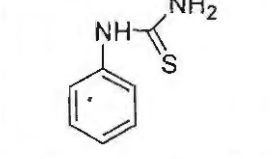
INTRODUCTION

Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid decaling and oil well acidizing. Because of the general aggressivity of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Most of the well-known acid inhibitors are organic compounds containing N, O, P, S and aromatic ring or triple bonds. It was reported before that the inhibition efficiency decreases in the order: O < N < S < P [Babu *et al.*, (2005); Fouda *et al.*, (2005); Yurchenko *et al.*,

(2006); Hossain *et al.*, (2006)]. In general, organic compounds are effective inhibitors of aqueous corrosion of many metals and alloys. The use of chemical inhibitors to decrease the rate of corrosion processes of carbon steels is quite varied [Abd El-Wahaab *et al.*, (2007); Muralidharan *et al.*, (2006); Quraishi *et al.*, (1996); Bentiss *et al.*, (2001); Sahin *et al.*, (2003)]. A variety of organic compounds containing heteroatoms such as O, N, S and multiple bonds in their molecule are of particular interest as they give better inhibition efficiency than those containing N or S alone [Lebrini *et al.*, (2006); Lebrini *et al.*, (2007)]. Sulfur and/or nitrogen containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors. Hydrazide derivatives offer special affinity to inhibit corrosion of metals in acid solutions [Abd El-Hamid *et al.*, (2004); Tsuru *et al.*, (1978); Mohamed *et al.*, (2000); El-Ouafi *et al.*, (2002)]. Azoles have been intensively investigated as effective steel corrosion [Aramaki *et al.*, (1987); Larabi *et al.*, (2004); Aramaki *et al.*, (1987); Ochoa *et al.*, (2004); Bentiss *et al.*, (2002); Aramaki *et al.*, (1969)]. The aim of the present work is to study the inhibition efficiency of the new synthesized thiourea derivatives on the corrosion of C-steel in 2 M HCl solution using electrochemical techniques. Previously, some thiourea compounds were used as corrosion inhibitors for some metals and alloys [S.M.A. Hosseini *et al.*, (2009); A. A. Khadom *et al.*, (2009) A.M. Fekry *et al.*, (2010)].

EXPERIMENTAL TECHNIQUES

2 M HCl solutions were prepared from an analytical reagent grade of HCl 98% and bi-distilled water and were used as corrosive media in this study. All the experiments were performed at 298 ± 1 K with C- steel samples containing (weight %): 0.200% C, 0.350% Mn, 0.024% P, 0.003% Si and the remainder iron. The inhibitors were synthesized in the laboratory [Abd El-Hamid *et al.*, (2004)] by reacting equimolecular mixture of the respective phenol derivative and thiourea derivative in 100 ml boiling ethanol. The mixture was refluxed on water bath for 2-6 hrs and the solution was evaporated to about its half volume, left to cool where crystals were separated out. These were filtered off, recrystallized from ethanol and finally dried in vacuum desiccator over anhydrous CaCl_2 . The compound structures were confirmed by elemental analysis and IR and nuclear magnetic resonance (NMR) spectroscopy. The investigated thiourea derivatives are:

Compound	Structure	Name	Mol. Formula Mol. Wt
1		1-(4-methoxyphenyl)- 3-phenylthiourea	$C_{14}H_{14}N_2OS$ 258.34
2		1-phenyl-3-p- tolylthiourea	$C_{14}H_{14}N_2S$ 242.34
3		1-(4-bromophenyl)-3- phenylthiourea	$C_{13}H_{11}BrN_2S$ 307.21
4		1-(4-chlorophenyl)-3- phenylthiourea	$C_{13}H_{11}ClN_2S$ 262.76
5		1-phenylthiourea	$C_7H_8N_2S$ 152.22

1. Potentiodynamic polarization method:

Electrochemical polarization experiments were carried out in a glass cell with a capacity of 250 ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. The working electrode was in the form of a disc with an exposed area of 0.12 cm^2 that was

cut from C- steel under investigation. A time interval of about 30 minutes was given for the system potentiodynamic to attain a steady state and the open circuit potential (OCP) was noted. Both cathodic and anodic polarization curves were recorded at $300 \text{ mV} \pm \text{OCP}$ and scan rate of 2 mV s^{-1} .

% IE was calculated using the equation:

$$\% IE = \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}} \times 100 \quad (1)$$

where: i_{corr} and i'_{corr} are the corrosion current densities in the absence and presence of the inhibitors, respectively.

2. Electrochemical impedance spectroscopy (EIS) method

EIS experiment were conducted at $303 \pm 1 \text{ K}$ at the OCP over a frequency range of 1 kHz to 1 Hz , with a signal amplitude perturbation of 10 mV using IM6e system (Zahner Elektrik, Germany) and personal computer. Nyquist plots were obtained from the results of these experiments. Values of the charge transfer resistance (R_{ct}) were obtained from these plots by determining the difference in the values of impedance at low and high frequencies, as suggested by Tsuru et al [Tsuru et al.(1978)]. Values of the double layer capacitance (C_{dl}) were calculated from the frequency at which the impedance imaginary component ($-Z''$) was maximum, using the following equation:

$$f(-Z''_{\text{max}}) = \frac{1}{2\pi C_{\text{dl}} R_{\text{ct}}} \quad (2)$$

% IE was calculated using the equation:

$$\% IE = \frac{(1/R'_{\text{ct}}) - (1/R_{\text{ct}})}{(1/R'_{\text{ct}})} \times 100 \quad (3)$$

where: R'_{ct} and R_{ct} are the charge transfer resistance values in the absence and presence of the inhibitors, respectively.

RESULTS

1. Potentiodynamic polarization:

Potentiodynamic anodic and cathodic polarizations were carried out in unstirred 2 M HCl solution in the absence and presence of various concentrations of the inhibitors (1-5) at 303 K over potential range $300 \text{ mV} \pm \text{OCP}$. The results are represented in Fig. (1) for compound (1), similar behaviors were obtained for other compounds. The obtained corrosion parameters are given in Table (1). These results indicate that the cathodic and anodic curves obtained exhibit Tafel-type behavior. Additionally, the form of these curves is very similar either in the cathodic or in the anodic side, which

indicates that the mechanisms of carbon steel dissolution and hydrogen reduction apparently remain unaltered in the presence of these additives. Addition of thiourea compounds decreased both the cathodic and anodic current densities and caused mainly parallel displacement to the more negative and positive values, respectively, i.e. the presence of thiourea derivatives in solution inhibits both the hydrogen evolution and the anodic dissolution processes with overall shift of E_{corr} to more negative values with respect to the OCP, this indicates that thiourea compounds acts as cathodic inhibitors.

The results also show that the slopes of the anodic and the cathodic Tafel slopes (β_a and β_c) were slightly changed on increasing the concentration of the tested compounds. This indicates that there is no change of the mechanism of inhibition in presence and absence of inhibitors. The fact that the values of β_c are slightly higher than the values of β_a suggesting a cathodic action of the inhibitor. This could be interpreted as an action of mixed inhibitor control over the electrochemical semi-reactions. This means that the thiourea derivatives are mixed type inhibitors, but the cathode is more preferentially polarized than the anode. The higher values of Tafel slope can be attributed to surface kinetic process rather the diffusion-controlled process [Mohamed *et al.*, (2000)]. The constancy and the parallel of cathodic slope obtained from the electrochemical measurements indicate that the hydrogen evolution reaction was activation controlled [El-Ouafi *et al.*, (2002)] and the addition of these derivatives did not modify the mechanism of this process. This result suggests that the inhibition mode of the thiourea derivatives used was by simple blockage of the surface by adsorption. The order of decreased inhibition efficiency for the additives is:

$$1 > 2 > 3 > 4 > 5$$

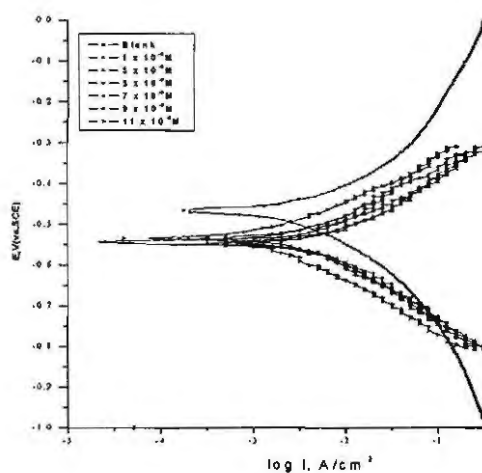


Fig.(1) Potentiodynamic polarization curve of carbon steel in 2 M HCl in the absence and presence of different concentrations of compound 1 at 30 °C.

Table (1): Corrosion parameters obtained from potentiodynamic polarization of C-steel in 2M HCl containing various concentrations of inhibitors at 30 °C.

Comp	Conc., $\times 10^6$ M	$-E_{\text{corr}}$, mV vs. SCE	i_{corr} mA cm^{-2}	θ	% IE_{icor}	β_c mVdec^{-1}	β_a mVdec^{-1}	R_p Ωcm^2	% IE_{R_p}
Blank	0.0	468	9.207	---	---	306	270	8.943	---
1	1	555	8.416	0.082	8.2	158	151	7.106	8.1
	3	548	7.306	0.206	20.6	163	133	6.902	22.8
	5	545	5.974	0.351	35.1	149	158	5.703	36.2
	7	537	5.401	0.413	41.3	154	121	5.302	40.7
	9	533	4.683	0.491	49.1	135	119	4.603	48.5
	11	532	1.529	0.833	83.3	131	103	1.308	85.3
2	1	551	8.753	0.054	5.4	164	143	8.282	7.3
	3	549	7.914	0.140	14.0	160	128	7.436	16.8
	5	549	6.579	0.255	25.5	163	126	6.091	31.8
	7	545	5.671	0.384	38.4	154	128	5.236	41.4
	9	542	4.938	0.463	46.3	130	121	4.662	47.8
	11	522	3.149	0.658	65.8	129	103	1.894	78.8
3	1	552	8.896	0.033	3.3	171	143	8.442	5.6
	3	544	7.996	0.131	13.1	166	147	7.536	15.7
	5	541	6.714	0.270	27.0	160	136	6.294	29.6
	7	548	5.763	0.374	37.4	157	129	5.493	38.5
	9	553	5.038	0.452	45.2	140	119	4.716	47.2
	11	537	4.617	0.498	49.8	143	107	4.287	52.0
4	1	541	8.999	0.022	2.2	158	166	7.504	1.6
	3	542	7.996	0.131	13.1	161	141	7.563	15.4
	5	552	6.748	0.267	26.7	147	138	6.321	29.3
	7	543	5.873	0.362	36.2	153	127	5.603	37.3
	9	547	5.111	0.444	44.4	139	131	5.027	43.8
	11	542	4.691	0.490	49.0	150	129	4.462	50.1
5	1	550	9.012	0.021	2.1	163	149	7.544	1.5
	3	549	8.079	0.122	12.2	160	137	7.593	15.0
	5	548	7.803	0.152	15.2	165	131	6.706	25.0
	7	544	6.889	0.251	25.1	158	125	5.889	34.1
	9	550	6.416	0.303	30.3	137	114	5.103	42.9
	11	527	5.036	0.453	45.3	134	102	4.548	49.1

1.1. Synergistic effect :

The effect of addition 1×10^{-2} M KSCN, KI and KBr on the corrosion rate of C- steel in the absence and presence of different concentrations of inhibitors (1-5) in 2M HCl solutions was investigated using potentiodynamic polarization method. Results of % IE of KI obtained are summarized in Table 2. It was observed from these results that these additives improved the % IE significantly. The interactions of these additives with the inhibitor molecules can be described by introduction of the synergistic parameter (S_θ) which is defined as [Aramaki *et al.*, (1987)]:

$$S_\theta = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \quad (4)$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$

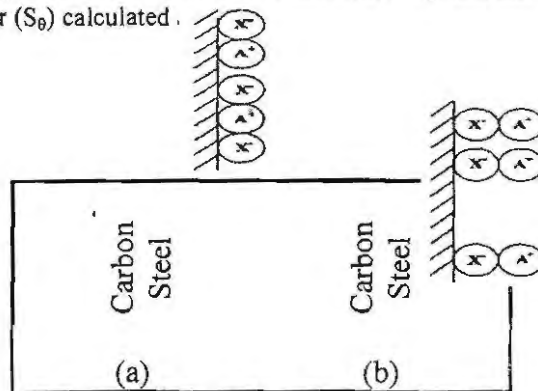
θ_1 = the degree of surface coverage by the anions

θ_2 = the degree of surface coverage by the cations

θ'_{1+2} = measured surface coverage by both anions and cations.

S_θ approaches 1 when no interaction between the inhibitor compounds exists, while $S_\theta > 1$ points to a synergistic effect. In the case of $S_\theta < 1$, the antagonistic interaction prevails.

Plot of synergism parameter S_θ vs. concentration of inhibitor of compound (1) with addition of KI is given in fig.(2) and values of S_θ summarized in Table (3) are more than unity, suggesting that the phenomenon of synergism exists between the inhibitors and these additives used. Aramaki [Larabi *et al.*, (2004); Aramaki *et al.*,(1987)] has proposed two kinds of joint adsorption (competitive and cooperative) to explain the synergistic action observed between an anion and a cation [Ochoa *et al.*,(2004)]. For competitive adsorption, the anion and cation are adsorbed at different sites on the electrode surface and for cooperative adsorption, the anion is chemisorbed on the surface and the cation is adsorbed on the layer of the anions. The two types of adsorption are represented schematically in following Fig. and can be characterized by a synergistic factor (S_θ) calculated .



Schematic representations of (a) competitive and (b) cooperative adsorption of the anions (X^-) and cations (A^+) on carbon steel surface in acid solutions.

Table (2) : Corrosion parameters obtained from potentiodynamic polarization of carbon steel in 2 M HCl containing various concentrations of inhibitor in the presence of 1×10^{-2} M KI at 30 °C.

Comp	Conc., $\times 10^4$ M	$-E_{\text{corr}}$ mV vs SCE	i_{corr} mA cm^{-2}	θ	% IE_{corr}	β_c mVdec^{-1}	β_a mVdec^{-1}	R_p $\Omega \text{ cm}^2$	% IE_{R_p}
Blank	0.0	468	9.207	----	---	306	270	8.943	----
1	1	544	8.302	0.098	9.8	160	142	7.043	21.2
	3	547	7.216	0.216	21.6	162	140	6.779	24.1
	5	546	5.906	0.358	35.8	143	159	5.199	37.3
	7	539	5.299	0.424	42.4	150	121	5.306	41.8
	9	536	4.399	0.522	52.2	137	126	4.499	49.6
	11	535	1.013	0.889	88.9	129	108	0.861	90.3
2	1	551	8.317	0.096	9.6	163	149	7.049	21.1
	3	550	7.249	0.212	21.2	160	137	6.801	23.9
	5	549	5.917	0.357	35.7	159	131	5.603	37.3
	7	545	5.302	0.442	42.4	152	128	5.207	41.7
	9	551	4.401	0.521	52.1	133	115	4.502	49.6
	11	532	1.096	0.880	88.0	131	102	0.879	90.1
3	1	552	8.337	0.094	9.4	171	142	7.053	21.1
	3	542	7.263	0.211	21.1	167	139	6.842	23.4
	5	542	5.948	0.353	35.3	153	125	5.624	37.1
	7	546	5.346	0.419	41.9	157	127	5.229	41.5
	9	556	4.423	0.519	51.9	129	114	4.537	52.49.2
	11	538	31.102	0.880	88.0	141	109	0.893	90.0
4	1	544	8.352	0.098	9.8	156	162	7.064	21.0
	3	546	7.299	0.207	20.7	163	134	6.873	23.1
	5	558	5.978	0.350	35.0	145	135	5.667	36.6
	7	541	5.377	0.415	41.5	151	121	5.278	40.9
	9	547	4.467	0.514	51.4	137	122	4.570	48.8
	11	547	1.167	0.873	87.3	147	113	0.901	89.9
5	1	552	8.367	0.091	9.1	162	151	7.081	20.8
	3	547	7.316	0.205	20.5	160	138	6.899	22.8
	5	552	6.001	0.348	34.8	163	131	5.693	36.3
	7	548	5.398	0.413	41.3	159	127	5.294	40.8
	9	546	4.489	0.512	51.2	129	115	4.587	48.7
	11	519	1.197	0.869	86.9	137	104	0.935	89.5

The synergistic inhibitive effect brought about by combination of the inhibitors with KSCN, KI and KBr for the corrosion of C- steel in 1 M HCl can be explained as follows: The strong chemisorption of X^- ions (SCN^- , I^- or Br^-) on the metal surface is responsible for the synergistic effect of these ions, in attraction with protonated inhibitor [Aramaki et al.,(1987)]. X^- ions are adsorbed on the anodic sites on the metal surface. Surface charge is changed to negative by the specific adsorption of these ions resulting in the joint adsorption of anions with the inhibitor cations. The inhibitors are believed to be adsorbable, not only on the cathodic sites by coulombic attraction using the charge of the protonated molecule, but also on the anodic sites by virtue of donation of the electron-pair on the nitrogen atom of the unprotonated molecule [Aramaki et al.,(1969)] therefore, interference adsorption can take place at the anodic sites.

Table(3) : Synergism parameter (S_0) for different concentrations of investigated compounds for carbon steel dissolution in 2 M HCl with addition of 1×10^{-2} M KI at 30 °C.

Conc., M	Synergism parameter (S_0)				
	(1)	(2)	(3)	(4)	(5)
1×10^{-6}	1.0	1.1	1.0	1.1	1.0
3×10^{-6}	1.2	1.1	1.1	1.1	1.1
5×10^{-6}	1.1	1.0	1.3	1.2	1.0
7×10^{-6}	1.3	1.0	1.0	1.0	1.2
9×10^{-6}	1.2	1.0	1.1	1.0	1.0
11×10^{-6}	1.2	1.2	1.2	1.3	1.1

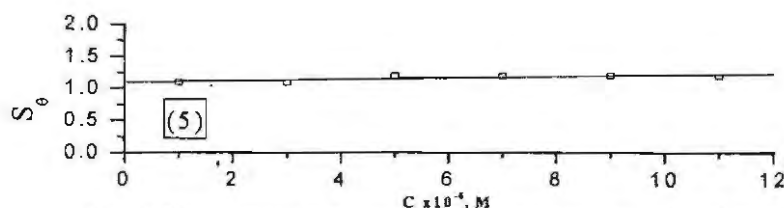


Fig. (2): Plots of synergism parameter (S_0) versus concentrations of inhibitors for C-Steel dissolution in 2M HCl with addition of 1×10^{-2} M KI at 30°C.

1.2. Adsorption isotherm :

Assuming the corrosion inhibition was caused by the adsorption of thiourea derivatives, and the values of surface coverage for different concentrations of inhibitors

in 2 M HCl were evaluated from potentiodynamic polarization method using equation(1):

From the values of (Θ) , it can be seen that the values of (Θ) increased with increasing the concentration of thiourea derivatives. Using these values of surface coverage, one can utilize different adsorption isotherms to deal with experimental data. The Temkin adsorption isotherm was applied to investigate the adsorption mechanism, by plotting (Θ) Vs $\log C$, and straight lines were obtained (Fig.3). On the other hand, it is found that Kinetic- thermodynamic model of [El-Awady *et al*] which has the formula:

$$\text{Log } (\Theta/1 - \Theta) = \text{log } K' - y \text{ log } C \quad (5)$$

Table (4): Inhibitor equilibrium constant (K), free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$), number of active sites (1/y) and the interaction parameter (a) for inhibitor additives at 30°C

Inhibitors	Kinetic model			Temkin		
	1/y	K	$-\Delta G^{\circ}_{\text{ads}}$ kJmol ⁻¹	a	K	$-\Delta G^{\circ}_{\text{ads}}$ kJmol ⁻¹
(1)	3.04	0.899	59.2	13.99	71.0	62.0
(2)	3.21	0.858	57.8	13.03	66.3	61.9
(3)	3.07	0.676	53.4	12.96	16.2	51.8
(4)	2.03	0.601	51.3	12.67	3.03	38.0
(5)	2.12	0.443	47.2	12.34	2.02	32.1

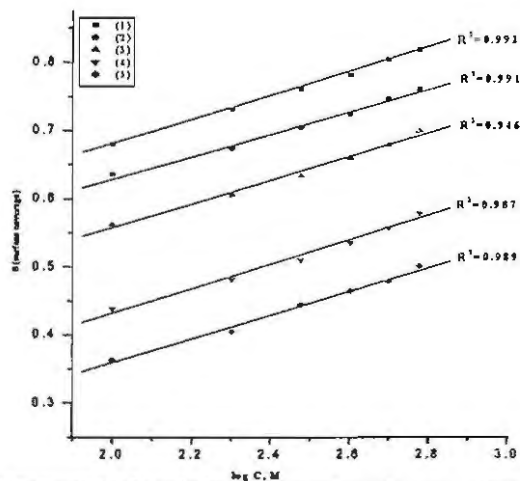


Fig. (3): Curve fitting of corrosion data for C-Sierr in 2 M HCl in presence of different concentrations of inhibitors corresponding to Temkin adsorption isotherm at 30 °C.

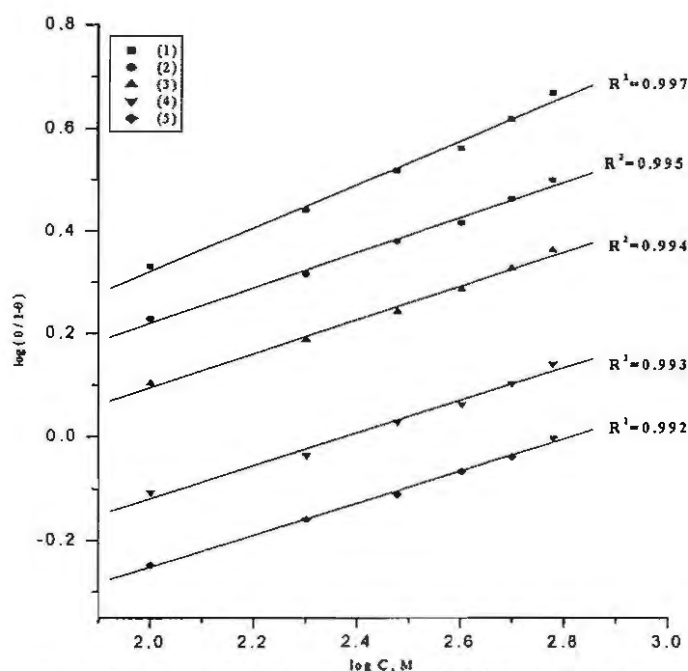


Fig. (4): Curve fitting of corrosion data for C-Steel in 2 M HCl in presence of different concentrations of inhibitors to the kinetic model at 30 °C.

is valid and verify the present adsorption data Fig.(4). The equilibrium constant of adsorption $K = K^{(1/y)}$, where $1/y$ is the number of the surface active sites occupied by one aldehyde molecule and C is the bulk concentration of the inhibitor.

The thermodynamic parameters for the adsorption process that were obtained from these Figures are shown in Table (4). The values of ΔG_{ads} are negative and increased as the % IE increased which indicate that these investigated compounds are strongly adsorbed on the C- steel surface and show the spontaneity of the adsorption process and stability of the adsorbed layer on the C-steel surface. Generally, values of ΔG_{ads} up to -20 kJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 kJ mol^{-1} involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorptions) [Bensajjay *et al.*,(2003)]. The values of ΔG_{ads} obtained were approximately equal to $-59.2 \pm 1 \text{ kJ mol}^{-1}$, indicating that the adsorption mechanism of the thiourea derivatives on C- steel in 2M HCl solution involves both electrostatic adsorption and chemisorptions [Duan *et al.*,(1990)]. The thermodynamic parameters point toward both physisorption (major contributor) and chemisorptions (minor contributor) of the inhibitors onto the metal surface. The K_{ads} follow the same trend in the sense that large values of K_{ads} imply better more efficient adsorption and hence better inhibition efficiency [Abd El-Rehim *et al.*,(2001)].

1.3. Effect of temperature :

Corrosion reactions are usually regarded as Arrhenius processes and the rate (k) can be expressed by the relation:

$$\text{Rate } (k) = A \exp (-E_a^*/RT) \quad (6)$$

where: E_a (kJ mol^{-1}) is the activation energy of the corrosion process R ($8.134 \text{ J mol}^{-1} \text{ K}^{-1}$) is the universal gas constant, T (K) is the absolute temperature and A is a Arrhenius pre-exponential constant depends on the metal type and electrolyte. Arrhenius plots of $\log k$ vs. $1/T$ for carbon steel in 2 M HCl in the absence and presence of 9×10^{-6} M concentration of inhibitors are shown graphically in Fig. (5). The variation of $\log k$ vs. $1/T$ is a linear one and the values of E_a obtained are summarized in Table (5). These results suggest that the inhibitors are similar in the mechanism of action. The increase in E_a with the addition of concentration of inhibitors (1-5) indicating that the energy barrier for the corrosion reaction increases. It is also indicated that the whole process is controlled by surface reaction, since the activation energy of the corrosion process is over 20 kJ mol^{-1} [Al-Neami *et al.*, (1995)].

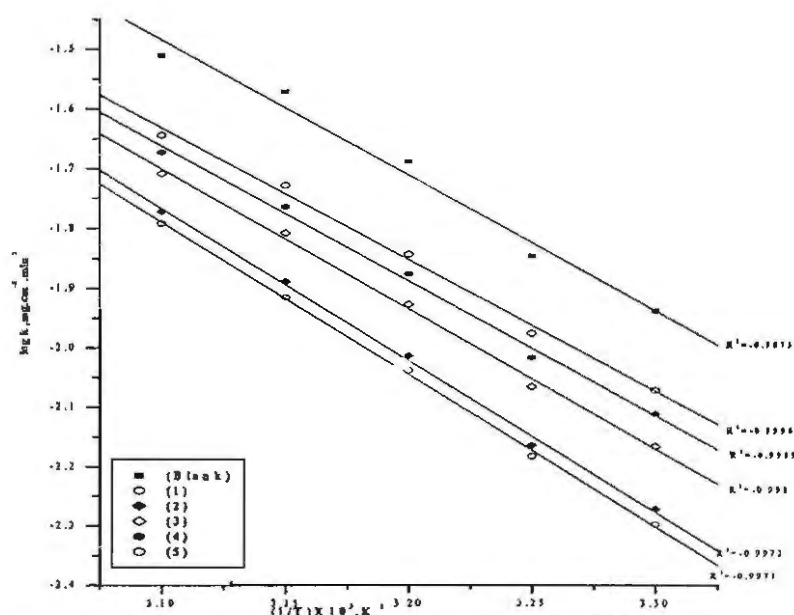
Enthalpy and entropy of activation (ΔH^* , ΔS^*) are calculated from transition state theory using the following equation [Haladky *et al.*, (1980)]:

$$\text{Rate } (k) = (RT/Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \quad (7)$$

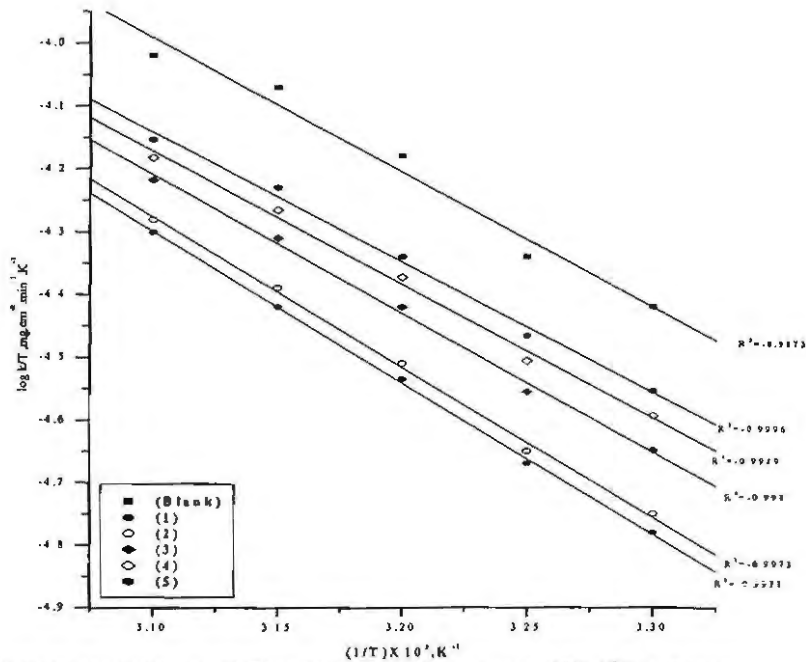
where: h is Plank's constant, N is Avogadro's number. A plot of $\log k/T$ vs $1/T$ also gave straight lines as shown in Fig. (6) for carbon steel in 2 M HCl in the absence and presence of 9×10^{-6} M concentration of inhibitors. The slopes of these lines equal $-\Delta H^*/2.303R$ and the intercept equal $\log RT/Nh + (\Delta S^*/2.303R)$ from which the value of ΔH^* and ΔS^* were calculated and tabulated in Table (5). From these results, it is clear that the presence of the tested compounds increased the activation energy values and consequently decreased the corrosion rate of the carbon steel. These results indicate that these tested compounds acted as inhibitors through increasing activation energy of carbon steel dissolution by making a barrier to mass and charge transfer by their adsorption on carbon steel surface. The values of ΔH^* reflect the strong adsorption of these compounds on carbon steel surface. The values of ΔS^* in absence and presence of the tested compounds are large and negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that a decreases in disordering takes place on going from reactants to the activated complex and the activated molecules were in higher order state than that at the initial state [Abd El-Rehim *et al.*, (1999); Fouda *et al.*, (2006)].

Table (5): Activation parameters for the dissolution of carbon steel in 2 M HCl acid solution in the absence and presence of 9×10^{-6} M of phenylthiourea derivatives

Inhibitor	Activation parameters		
	E_a^* , kJ mol ⁻¹	ΔH^* , kJ mol ⁻¹	$-\Delta S^*$, J mol ⁻¹ K ⁻¹
Blank	42.4	40.01	153.6
1	48.1	46.1	135.4
2	47.9	44.2	136.1
3	43.8	42.3	145.8
4	42.2	41.0	150.3
5	41.2	40.0	152.8



Fig(5): log corrosion rate(k) vs. 1/T for C-steel in presence of 9×10^{-6} M Compounds.



Fig(6): log corrosion rate/ $T(k/T)$ vs. $1/T$ for C-steel in presence of $9 \times 10^{-4} M$ compounds.

2. Electrochemical Impedance Spectroscopy :

Impedance diagram (Nyquist) at frequencies ranging from 1 Hz to 1 kHz with 10 mV amplitude signal at OCP for carbon steel in 2 M HCl in the absence and presence of different concentrations of compounds (1-5) are obtained. The equivalent circuit that describes our metal/electrolyte interface is shown in Fig. (7) where R_s , R_{ct} and CPE refer to solution resistance, charge transfer resistance and constant phase element, respectively. EIS parameters and % IE were calculated and tabulated in Table 6. In order to correlate impedance and polarization methods, i_{corr} values were obtained from polarization curves and Nyquist plots in the absence and presence of different concentrations of compounds (1-5) using the Stern-Geary equation:

$$i_{corr} = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c) R_{ct}}$$

The obtained Nyquist plot for compound (I) is shown in Fig.(8) Each spectrum is characterized by a single full semicircle. The fact that impedance diagrams have an approximately semicircular appearance shows that the corrosion of carbon steel is controlled by a charge transfer process. Small distortion was observed in some diagrams, this distortion has been attributed to frequency dispersion [Mansfeld *et al.*, (1982)]. The diameters of the capacitive loop obtained increases in the presence of

thiourea derivatives, and were indicative of the degree of inhibition of the corrosion process [Mansfeld *et al.*, (1990)].

Table (6) : Electrochemical kinetic parameters obtained from EIS technique for the corrosion of carbon steel in 2 M HCl at different concentrations of inhibitor1 at 30 °C.

Conc., M	C_{dl} , $\mu F\ cm^{-2}$	R_{ct} , $\Omega\ cm^2$	Θ	% IE
Blank	98.02	19.03	----	----
5×10^{-6}	96.36	27.43	0.296	29.6
7×10^{-6}	94.74	44.77	0.569	56.9
9×10^{-6}	90.03	85.03	0.773	77.3
11×10^{-6}	86.90	122.06	0.842	84.2

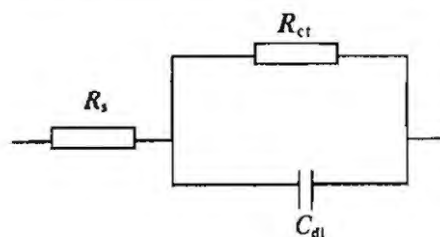
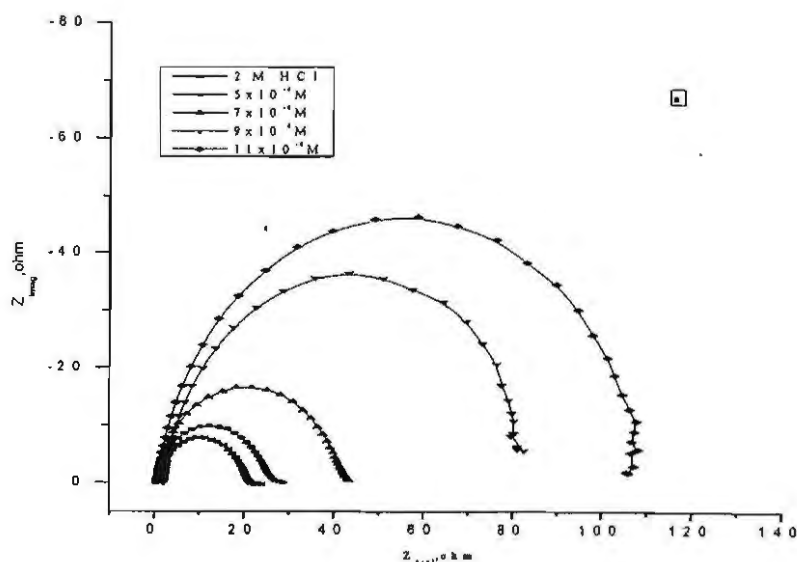


Fig. (7) : Equivalent circuit of constant phase element (CPE).



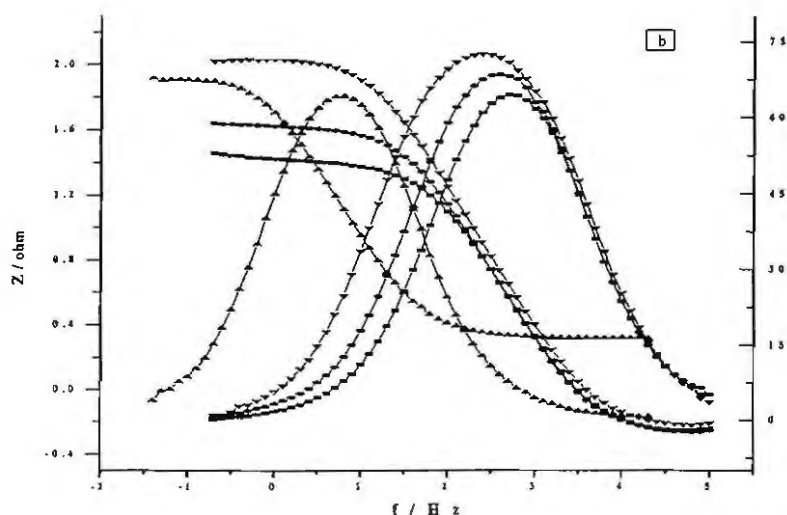


Fig. (8). The Nyquist (a) and Bode (b) plots for corrosion of C-steel in 2M HCl in the absence and presence of different concentrations of compound (1) at 30°C.

It was observed from the obtained EIS data that R_{ct} increases and C_{dl} decreases with the increasing of inhibitor concentrations. The increase in R_{ct} values, and consequently of inhibition efficiency, may be due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface to form an adherent film on the metal surface. And this suggests that the coverage of the metal surface by the film decreases the double layer thickness. Also, this decrease of C_{dl} at the metal/solution interface with increasing the inhibitor concentration can result from a decrease in local dielectric constant which indicates that the inhibitors were adsorbed on the surface at both anodic and cathodic sites [McCafferty *et al.*, (1972)].

The impedance data confirm the inhibition behavior of the inhibitors obtained with other techniques. From the data of Table (6), it can be seen that the i_{corr} values decrease significantly in the presence of these additives and the % IE is greatly improved. The order of reduction in i_{corr} exactly correlates with that obtained from potentiostatic polarization studies. Moreover, the decrease in the values of i_{corr} follows the same order as that obtained for the values of C_{dl} . It can be concluded that the inhibition efficiency found from polarization curves, electrochemical impedance spectroscopy measurements and the Stern-Geary equation are in good agreement.

3. Chemical-quantum calculations :

Table (7) shows the energy (in eV) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for inhibitors. It has been reported that the higher the HOMO energy (E_{HOMO}) level of the inhibitor, the

greater is the ease of offering electrons to unoccupied d orbital of metallic iron and the greater the inhibition efficiency [Ogretir et al.,(1999)]. The present results show that E_{HOMO} and E_{LUMO} decrease in the order: 1 > 2 > 3 > 4 > 5 which is parallel to the order of inhibition efficiency.

Table (7) The calculated quantum chemical properties for phenylthiourea compounds

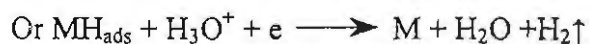
Quantum chemical parameters	Compounds				
	(1)	(2)	(3)	(4)	(5)
- E_{HOMO} (ev)	8.002	8.012	8.213	8.934	10.233
- E_{LUMO} (ev)	1.314	1.322	1.422	1.448	2.001
ΔE (kcal mol ⁻¹)	6.688	6.690	6.791	7.486	8.232
μ (Dipole moment)	3.025	4.223	6.043	9.025	11.014
Molecular weight	254.28	238.28	303.15	258.7	148.16

CORROSION INHIBITION MECHANISM

From the previous results of various experimental techniques used, it was concluded that thiourea derivatives (1-5) inhibit the corrosion of carbon steel in 2M HCl by adsorption at the metal/solution interface. A skeletal representation of the proposed mode of adsorption of studied compounds is shown in Fig. (9) and clearly indicates the active adsorption centers. The adsorption of these inhibitors can be explained in the following manner:



(discharge step) where: M is the cathode metal surface, followed by either:



(electrochemical desorption)

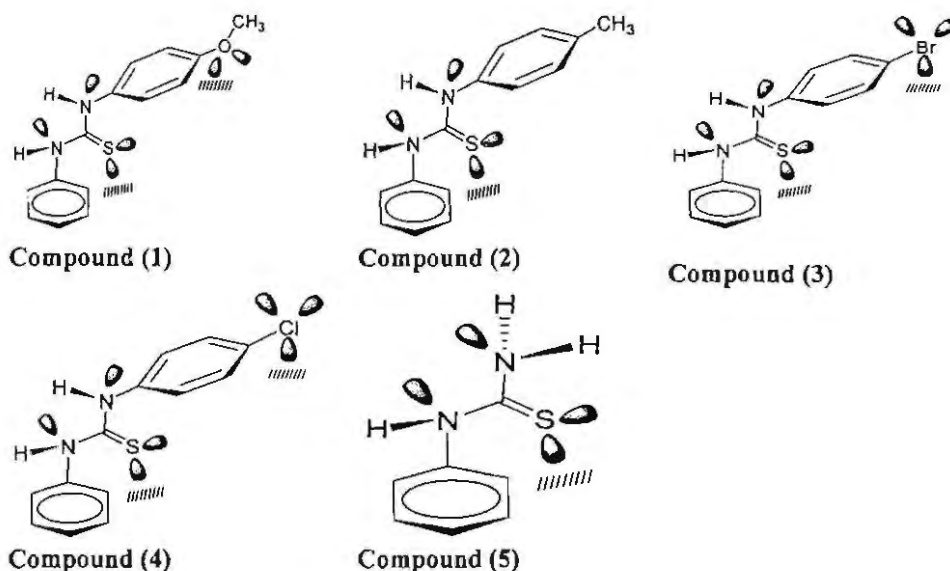


Fig. (9): Skeletal representation of the proposed adsorption of the thiourea additives on C-steel surface

Compound (1) exhibits excellent inhibition power due to: (i) the presence of *p*-OCH₃ group which is an electron donating group with negative Hammett constant ($\sigma = -0.27$), Also this group will increase the electron charge density on the molecule, (ii) its larger molecular size that may facilitate better surface coverage, and (ii) its adsorption through three active centers .

Compound (2) comes after compound (1) in inhibition efficiency due to: (i) its lower molecular size than compound (1), (ii) its adsorption through two active centers, and (iii) the presence of *p*-CH₃ with low Hammett constant than *p*-OCH₃ ($\sigma = -0.17$) which is highly electron releasing group which enhance the delocalized π -electrons on the active centers of the compound.

Compounds (3) and (4) come after compound (2) in percentage inhibition efficiencies. This is due to both *p*-Br and *p*-Cl groups are electron withdrawing groups with positive Hammett constants ($\sigma_{Br} = +0.23$, $\sigma_{Cl} = +0.23$) and their order of inhibition depends on the magnitude of their withdrawing character.

Compound (5) comes after compound (4) in inhibition efficiency inspite of it has three active centers, because it has lower molecular size than compound (4) and has no substituent in *p*-position which contributes no charge density to the molecule.

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الملخص العربي

دور بعض مشتقات الثيوبوريا كمثبطات لتآكل الصلب الكربوني في الوسط الحامضي
أ.د. عبد العزيز السيد فوده و أ.د. مصطفى أمين دياب و أحمد حسين سليمان

التآكل هو المشكله الرئيسيه التي تهدد فترة عمر صلاحية المعدن للإستخدام وفيهم ميكانيكية التآكل يمكننا من إيجاد حل لمشاكل التآكل الحاليه ومنع المشاكل المستقبلية وهذا البحث يناقش تآكل الصلب الكربوني في حمض الهيدروكلوريك وكيفية حمايته.

تم مناقشة التركيب الكيميائي لمركبات الثيوبوريا وتأثيرها على كفاءة تثبيط الصلب الكربوني في 2 مولر من حمض الهيدروكلوريك ولوحظ أن كفاءة تثبيط المركبات يعتمد على الشكل الفراغي للمركبات والمراكز النشطة الموجوده في المركبات التي تحدد الكثافه الإلكترونية على سطح الصلب الكربوني وكذلك التأثير القطبي للمجموعات المستبدله. وتمت الدراسات باستخدام الطرق التاليه:

(الإستقطاب البوتنشيوي ديناميكي والمعاقه الكهربيه)

ايضا تم حساب بعض القيم باستخدام تطبيقات الكم. وقد بينت النتائج ان المركبات المستخدمه تعمل كمثبط لكل من العملية الانودية والكاثودية. وقد وجد ان ادمصاص هذه المركبات يتبع ايزوثيوم تمكن. بزيادة درجة الحرارة يزداد معدل التآكل مما يدل على ان نوع الادمصاص هو ادمصاص فيزيائي ايضا تم حساب بعض الدوال الثيرموديناميكية. تمت دراسة التأثير التعاوني ليوديد وبرويد وثيوسيانات البوتاسيوم. خلاصة القول أن قياسات الإستقطاب الكهربيه تؤيد افتراضات أن تثبيط التآكل يتم عن طريق ادمصاص المثبطات على سطح الصلب الكربوني والإتفاق بين وسائل القياسات المختلفه في ترتيب كفاءة المثبطات المستخدمه وهذا يدل على صحة النتائج التي تم الحصول عليها.

