

Electrochemical, Activations and Adsorption Studies for the Corrosion Inhibition of Low Carbon Steel in Acidic Media

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Abstract

The effect of phenylthiourea as a corrosion inhibitor for low carbon steel at different hydrochloric acid concentrations, different temperatures and fixed speed of electrode rotation, were addressed in this work. Polarization technique was used to evaluate the corrosion rates parameters. The corrosion rate of low carbon steel increases with temperature and follows Arrhenius equation in all acid concentrations in presence and absence of the inhibitor. Detailed thermodynamic parameters of activation (ΔH_{act} and ΔS_{act}) for the corrosion reaction were obtained using nonlinear estimation method, while adsorption parameters (ΔG_{ads} , ΔH_{ads} and ΔS_{ads}) were obtained using graphical method. Maximum inhibitor efficiency was (96.44%) obtained at 1 M HCl at 333 K and 1 g/L inhibitor concentration.

Keywords: corrosion, low carbon steel, adsorption, activation parameters.

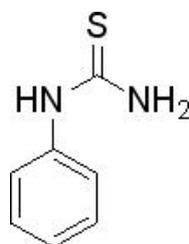
Introduction

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric acids are widely used in the pickling processes of metals. Use of inhibitors is one of the most practical methods for protection against corrosion, especially in acid solutions, to prevent metal dissolution and acid consumption [1]. The use of organic compounds containing oxygen, sulphur and nitrogen to reduce corrosion attack on steel has been studied in some details [2–5]. Sulphur and nitrogen containing compounds are more effective as corrosion inhibitors in hydrochloric acid [6].

The existing data show that most organic inhibitors get adsorbed on the metal surface by displacing water molecules and form a compact barrier film [7]. The availability of lone pairs and π electrons in the inhibitor molecules facilitates the

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electron transfer from the inhibitor to the metal, forming a coordinate covalent bond [8]. The strength of the adsorption bond depends on the electron density, on the donor atom of the functional group and also on the polarisability of the group. Thiourea and its derivatives are widely used as acid inhibitors in industrial operations, such as pickling, descaling, cleaning, acidification of oil wells, to protect metals and alloys [9]. The corrosion inhibitor acts as a protective film and is superior to amine-based inhibitors in acidic media. This kind of inhibitor simultaneously acts in both anodic and cathodic areas. The organic substances belonging to this group contain mainly oxygen, sulfur, nitrogen atoms, and multiple bonds in the molecules that facilitate the adsorption on the metal surface [10]. Sulfur compounds, such as thiourea derivatives, are very effective corrosion inhibitors for steel in acidic conditions because of sulfur atom is easily protonated in acidic solution and a stronger electron donor than nitrogen. Therefore, sulfur atom is more strongly adsorbed to the metal surface [11]. The molecular structure of phenylthiourea (PTU) is as follows:



In this work the inhibitive behavior of phenylthiourea on low carbon steel in 1, 3 and 5 M HCl solution at different temperatures and fixed speed of rotation has been studied.

Experimental work

Description of the system and materials

Samples of cylindrical shape with outside diameter of 1.96 cm and a length of 0.5 cm, of low carbon steel were used. The specimens were first degreased with analar benzene and acetone, and then annealed in a vacuum oven at 600 °C for 1 hour, and cooled to room temperature. Samples were abraded in sequence under running tap water using emery paper of grad number 220, 320, 400 and 600, then washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, and then kept in desiccators over silica gel bed until time of use. The corrosion cell has four necks: one was fitted with the working electrode, other one for immersing a thermometer in order to observe the test temperature, and the third one had a spherical joint for manipulating the lugging capillary probe. The probe was adjusted to be in a distance not more than 2 mm from the working electrode. The fourth neck input a graphite electrode. All potential values were measured in reference to saturated calomel electrode (SCE). DC power supply which is equipped with current and voltage limiters offers better stability and control, its type is 6236B, triple output supply Hewlet Packard, USA. In the present work, the corrosion reaction of low

carbon steel in 1, 3, and 5 M HCl, at 303, 313, 323, and 333 K, in presence of 0.1, 0.75, and 1 g/L phenylthiourea (PTU) as a corrosion inhibitor at fixed speed of rotation for specimens of 600 rpm, were studied. The low carbon steel working electrode specimens have the following chemical composition: C 0.041 wt%, Mn 0.311 %, P 0.05 %, S 0.007% and the remainder is iron.

Experimental procedure

The polarization readings begin after reaching a corrosion potential variation over time equal to about 1 mV/min. The cathodic polarization readings are carried out beginning from a low potential of (-900 mV) until reaching the corrosion potential. The potential was changed by steps of (25 mV) and the current was recorded for each step with 1.5 minute intervals between steps. The anodic polarization readings start at a potential resulting in zero current density and is increased in steps of (25 mV) with the current recorded at each step and with 1.5 minute intervals until a potential of 400 mV above the corrosion potential is reached.

Result and discussions

Electrochemical polarization studies

Polarization behavior of low carbon steel in 1, 3 and 5 M HCl in the presence and absence of inhibitors is shown in Fig. (1-3). When the corroding metal is cathodically polarized, the following relationship is generally observed [12]:

$$i_{app} = i_{corr} \left(e^{\frac{\Delta E}{\beta_a}} - e^{-\frac{\Delta E}{\beta_c}} \right) \quad (1)$$

where i_{app} is the applied current density; i_{corr} is the corrosion current density; β_a and β_c are the anodic and cathodic Tafel slopes; and ΔE is the over potential reverted to the corrosion potential.

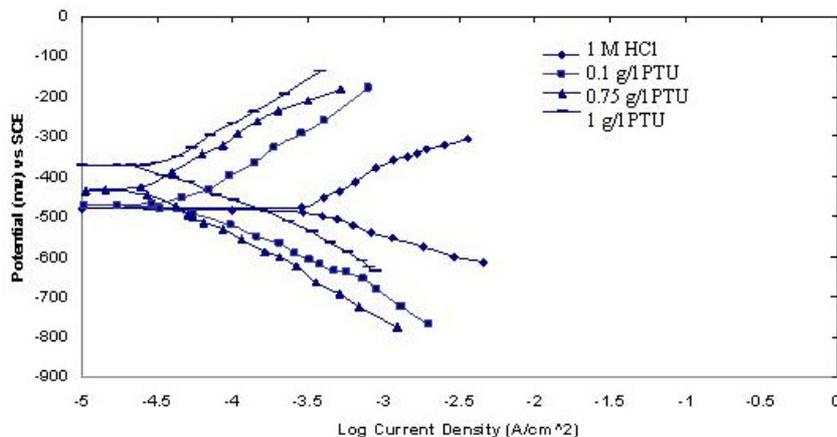


Figure 1. Polarization curves of low carbon steel in 1 M HCl and containing different inhibitor concentrations at 30 °C.

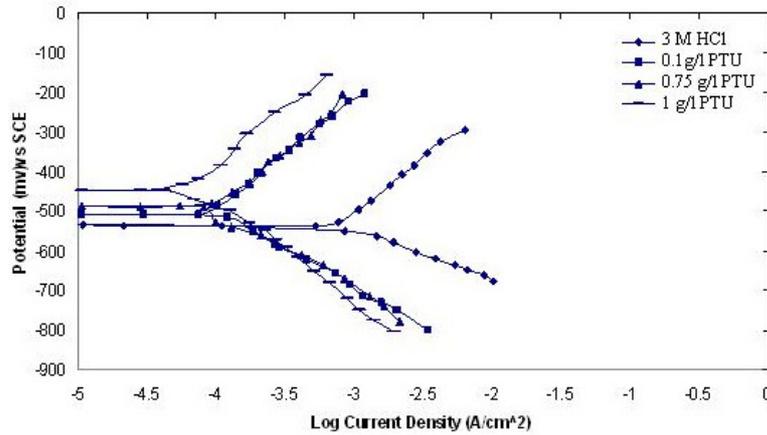


Figure 2. Polarization curves of low carbon steel in 3 M HCl and containing different inhibitor concentrations at 30 °C.

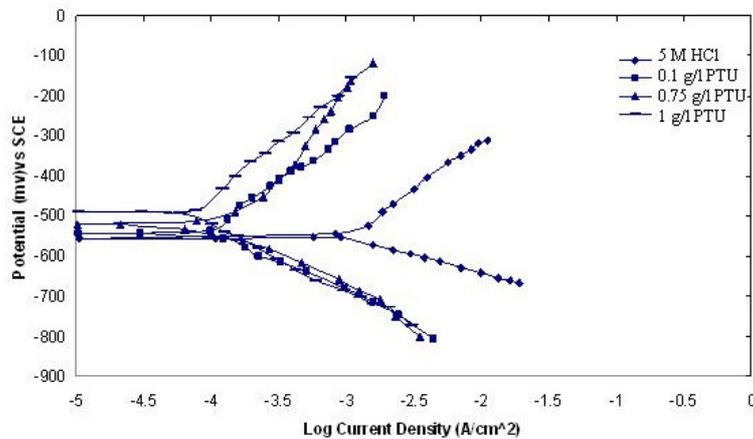


Figure 3. Polarization curves of low carbon steel in 5 M HCl and containing different inhibitor concentrations at 30 °C.

Equation (1) was used to determine numerically the unknown, i_{corr} , β_a , and β_c by simple computer program (BETACRUNCH program); this program can be used to calculate corrosion current density, i_{corr} , β_a and β_c from polarization data obtained from polarization figures by entering two sets of data for each condition, i.e., values of applied current density at ΔE equal to +20, +10, -10 mV and then +10, -10, -20 mV, in a total of two values of i_{corr} , β_a and β_c were obtained and the average of these values for every conditions was tabulated, as shown in Table 1, for acid solutions at different temperatures in presence and absence of the PTU as corrosion inhibitor.

The values of steady state corrosion potential (E_{corr}) were calculated after 1 hour immersion time, and these values with inhibition efficiency (IE %), are collected in Table 1. The relation determining the inhibition efficiency (IE %) is:

$$IE\% = \left(1 - \frac{i_{corr}}{i_{corr}^o}\right) \times 100 \quad (2)$$

where i_{corr}° and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

Table 1. Corrosion parameters at different conditions and fixed speed of rotation.

HCl (M)	PTU (g/L)	Temp (K)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	IE (%)
1	Blank	303	315.71	-480	55.73	63.91	
		313	1033.89	-492	53.08	54.11	
		323	1601.07	-570	46.74	47.54	
		333	2594.68	-522	52.62	53.05	
3		303	641.89	-535	49.25	51.78	
		313	1211.33	-576	70.95	71.55	
		323	6199.28	-550	95.97	97.99	
		333	5996.51	-580	67.51	69.11	
5		303	757.31	-555	40.38	42.38	
		313	3178.36	-589	70.95	71.55	
		323	9987.17	-593	104.67	105.89	
		333	10454.98	-610	78.57	79.13	
1	0.1	303	21.19	-471	40.83	50.85	93.21
		313	65.98	-489	47.17	61.71	93.61
		323	111.71	-470	43.57	49.28	93.02
		333	199.35	-472	63.83	74.64	92.31
3		303	91.55	-526	47.66	51.25	85.73
		313	111.34	-530	39.14	43.04	90.81
		323	903.89	-524	46.76	48.47	85.41
		333	1088.58	-570	35.11	35.43	81.84
5		303	125.05	-548	42.25	45.77	83.48
		313	399.23	-548	101.47	118.83	87.43
		323	2022.95	-549	52.21	52.71	79.7
		333	1840.71	-532	47.58	48.17	77.48
1	0.75	303	17.22	-425	44.94	53.29	94.54
		313	50.16	-430	73.68	83.67	95.14
		323	64.84	-421	41.74	49.16	95.96
		333	109.24	-430	33.41	34.09	95.78
3		303	51.46	-501	50.82	34.02	91.98
		313	85.65	-494	40.82	47.19	92.91
		323	576.15	-480	46.09	50.92	90.70
		333	876.04	-480	46.43	51.64	85.39
5		303	84.22	-529	40.53	43.09	88.87
		313	289.9	-500	88.74	99.08	90.87
		323	1576.41	-462	48.71	53.95	84.20
		333	1622.14	-469	61.78	73.83	82.39
1	1	303	14.93	-372	46.93	65.56	95.27
		313	42.93	-360	44.28	52.57	94.84
		323	58.77	-409	48.22	56.16	96.32
		333	92.3	-400	43.01	49.69	96.44
3		303	46.5	-450	42.07	46.62	92.75
		313	67.03	-445	48.73	56.89	94.40
		323	379	-420	43.64	46.32	93.88
		333	527	-452	38.18	42.92	91.21
5		303	70.69	-490	42.44	45.69	90.66
		313	229.39	-455	85.9	92.6	92.78
		323	1182.42	-432	49.62	51.85	88.16
		333	1354.15	-420	48.19	49.17	84.48

The corrosion potential is influenced directly by acid concentration, temperature of the acid solution and inhibitor concentration, as can be observed in Table 1. This means that at constant temperature of 303, 313, 323 and 333 K, the corrosion potential (in absence and presence of the inhibitor), shifts to more active direction (negative value) as the HCl concentration is increased. At constant acid concentration of 1, 3, and 5 M, the E_{corr} shifts to more negative direction as the temperature is increased from 303 to 333 K. This observation indicates that both acid concentration and temperature lead the system under investigation to be cathodically controlled in absence and presence of the inhibitor. Table 1 also shows that, at constant temperature level and constant acid concentrations level, the increased addition of the inhibitor at concentrations of 0.1 g/L to 1.0 g/L and 0.75 g/L renders and shifts the E_{corr} sharply toward more positive direction, indicating the effectiveness of PTU as inhibitor. Fig. (1-3) show that PTU inhibits both anodic and cathodic reactions, i.e., it is a mixed control inhibitor, the more relevant inhibition effect occurring on the anodic reaction. Puidori et al., Trabaneli et al. and Yamaok and Fischer [13] also found that PTU inhibits both anodic and cathodic reactions. From the examination of Fig. 1, 2 and 3 and Table 1, one can see that the addition of PTU reduces the current density. The reduction is more pronounced with the increase of the inhibitor concentration. Tafel plots indicate that the mechanism of hydrogen reduction is activation control. The presence of PTU does not affect the cathodic Tafel slope, indicating that the mechanism of H^+ reduction is not modified with the PTU concentration. The maximum inhibition efficiency was found to be (96.44%) at 1 M HCl, 333 K, and 1g/L inhibitor concentration, indicating that the efficiency of PTU is improved with temperature increasing.

Effect of temperature and activation studies

Thermodynamic parameters of the corrosion reaction, namely activation energy E_{act} , entropy ΔS_{act} and enthalpy ΔH_{act} of activation, were calculated using Arrhenius Eq. (3) and its alternative formulation called transition state Eq. (4). From the corrosion current densities obtained from polarization curves at different temperatures in absence and presence of PTU as corrosion inhibitor, Arrhenius plots were shown in Fig. (4 and 5) for a temperature range of (303-333 K) for a given acid concentration. Activation energies were calculated from the Arrhenius plots, which represent the relationship between $\log(i_{\text{corr}})$ and the reciprocal absolute temperature:

$$\log i_{\text{corr}} = \log A - \frac{E}{2.303RT} \quad (3)$$

While the transition state equation can be defined as:

$$i_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{\text{act}}}{R}\right) \exp\left(-\frac{\Delta H_{\text{act}}}{RT}\right) \quad (4)$$

where T is the absolute temperature, R is the universal gas constant, h is Plank's constant, and N is Avogadro's number. The values of entropy ΔS_{act} and of the

enthalpy ΔH_{act} of activation were obtained using nonlinear estimation of equation 3 with good regression coefficients which are listed in Table 2.

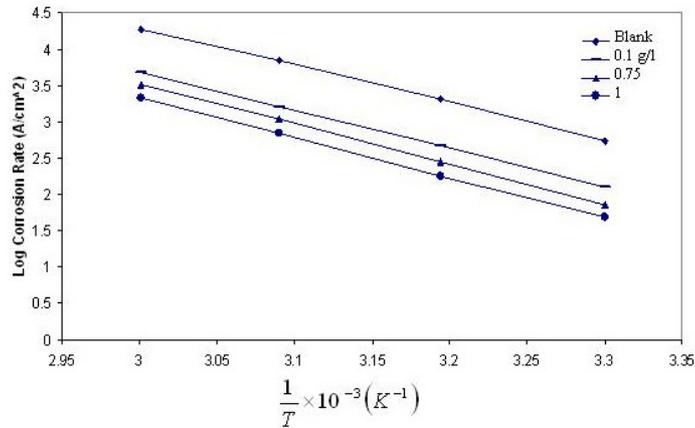


Figure 4. Arrhenius plots of low carbon steel in 3 M HCl and containing various concentrations of PTU as corrosion inhibitor at the temperature range of (303-333 K).

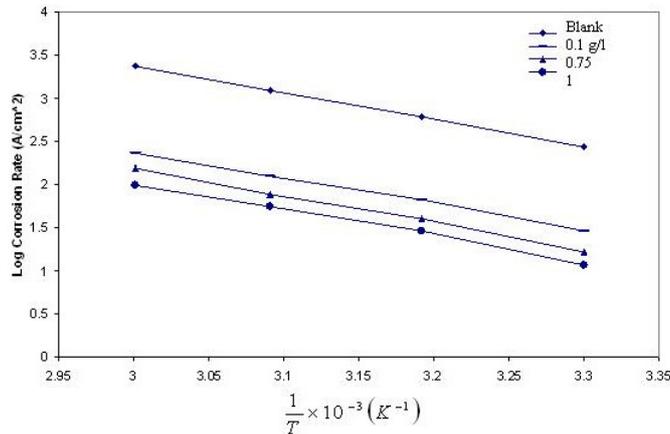


Figure 5. Arrhenius plots of low carbon steel in 5 M HCl and containing various concentrations of PTU as corrosion inhibitor at the temperature range of (303-333 K).

Table 2. Activation parameters for adsorption of PTU on low carbon steel surface at different conditions.

HCl (M)	PTU (g/L)	E_{act} (kJ.mol ⁻¹)	ΔH_{act} (kJ.mol ⁻¹)	ΔS_{act} (J.K ⁻¹ .mol ⁻¹)	Regression coefficient
1	Blank	68.45	43.66	-49.98	0.9901
3		60.18	42.62	-45.28	0.9612
5		48.61	42.59	-16.692	0.9771
1	0.1	76.19	50.18	-51.86	0.9962
3		66.29	53.35	-27.63	0.9152
5		49.52	42.17	-56.32	0.9390
1	0.75	76.82	39.54	-88.89	0.9840
3		67.87	42.55	-2.08	0.9627
5		50.52	46.89	-43.45	0.9797
1	1	78.26	38.09	-94.56	0.9854
3		77.64	56.32	-24.96	0.9531
5		56.23	50.01	-35.77	0.9123

The higher the acid solution concentration the lower the activation energy and activation enthalpy were recorded, indicating the dissolution process of the metal. This also indicates and means that the reaction at the metal surface requires a smaller activation energy and activation enthalpy to proceed when the acid solution concentration is increased. It is also observed that the activation energy E_{act} and activation enthalpy ΔH_{act} for uninhibited acid were lower than in inhibited acid. The higher values in the presence of PTU inhibitor indicate physical adsorption of the inhibitor on the metal surface.

The results showed positive sign for both E_{act} and ΔH_{act} , reflecting the endothermic nature of corrosion process. The values of E_{act} and ΔH_{act} vary in the same way; it is obviously seen that the activation energy strongly increases in the presence of the inhibitor. Some authors [14, 15, 16] attributed this result to the fact that the inhibitor species are physically adsorbed on the metal surface.

The negative values of ΔS_{act} pointed to a greater order produced during the process of activation. This can be achieved by the formation of activated complex and represents association or fixation with consequent loss in the degrees of freedom of the system during the process [17].

Adsorption isotherm studies

The primary step in the action of inhibitors in acid solution is generally agreed to be the adsorption on the metal surface. This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reactions occur normally on the inhibitor-free area [18]. Accordingly, the fraction of surface covered with inhibitor species ($\theta = IE\%/100$) can follow as a function of inhibitor concentration and solution temperature. The surface coverage (θ) data are very useful on discussing the adsorption characteristics. When the fraction of surface covered is determined as a function of the concentration at constant temperature, adsorption isotherm could be evaluated at equilibrium condition. The dependence of the fraction of the surface covered θ on the concentration C of the inhibitor was tested graphically by fitting it to Langmuir's isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. Fig. 6 shows the linear plots for C/θ versus C , suggesting that the adsorption obeys the Langmuir's isotherm:

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

where C is the inhibitor concentration, and K_{ads} the adsorptive equilibrium constant, representing the degree of adsorption (i.e., the higher value of K_{ads} indicates that the inhibitor is strongly adsorbed on the metal surface); the value of K_{ads} obtained from the reciprocal of intercept of Langmuir plot lines and the slope of these lines is near unity, meaning that each inhibitor molecule occupies one active site on the metal surface.

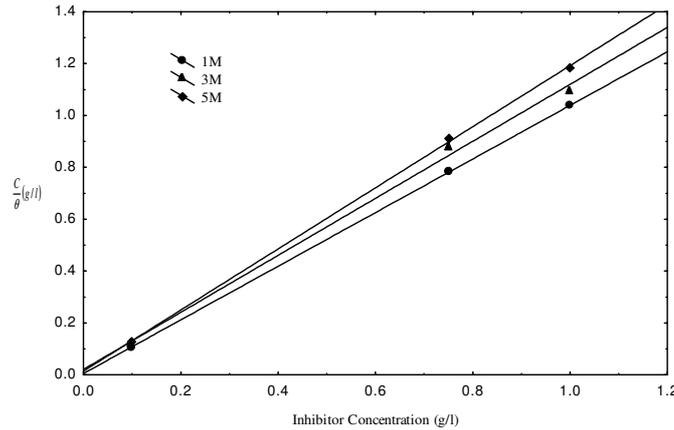


Figure 6. Langmuir adsorption isotherm of PTU on low carbon steel in different molarities of HCl solution at 60 °C.

Moreover, the essential characteristic Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L [19], which describes the type of isotherm and is defined by:

$$R_L = \frac{1}{1 + K_{ads} C} \tag{6}$$

The smaller R_L value indicates a highly favorable adsorption. If $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; and if $R_L = 0$, irreversible. Table 3 gives the estimated values of R_L for APTT at different concentrations. It was found that all R_L values are less than unity, confirming that the adsorption processes is are favorable.

The standard adsorption free energy (ΔG_{ads}^o) was calculated using the following equation [20]:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right) \tag{7}$$

where, 55.5 are the concentration of water in solution expressed in molar, R is the gas constant, and T the absolute temperature. The average value of standard adsorption free energy $\Delta G_{ads} = -22.796 \text{ kJ.mol}^{-1}$. The negative values of ΔG_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Generally, values of ΔG_{ads} up to -20 kJ.mol^{-1} are consistent with electrostatic interaction between the charged molecules and the charged metal (physisorption), while those around -40 kJ.mol^{-1} or higher are associated with chemisorptions as a result of sharing or transfer of electrons from the organic molecules to the metal surface to form a coordinate type of bond [21]. While other researchers suggested that the range of ΔG_{ads} of chemical adsorption processes for organic inhibitor in aqueous media lies between -21 to -42 kJ.mol^{-1} [22]. Therefore, for the present work the value of ΔG_{ads} has been considered within the range of physical adsorption.

Table 3. Dimensionless separation factor R_L for PTU at various concentrations.

Temperature (K)	HCl concentration (M)	PTU (g/L)	R_L	
303	1	0.1	0.0253	
		0.75	0.0034	
		1	0.0025	
	3	3	0.1	0.0360
			0.75	0.0049
			1	0.0037
	5	5	0.1	0.0421
			0.75	0.0058
			1	0.0043
313	1	0.1	0.0631	
		0.75	0.0089	
		1	0.0066	
	3	3	0.1	0.0856
			0.75	0.0123
			1	0.0092
	5	5	0.1	0.1113
			0.75	0.0164
			1	0.0123
323	1	0.1	0.1326	
		0.75	0.0199	
		1	0.0150	
	3	3	0.1	0.1769
			0.75	0.0278
			1	0.0210
	5	5	0.1	0.0913
			0.75	0.0132
			1	0.0099
333	1	0.1	0.1194	
		0.75	0.0177	
		1	0.0133	
	3	3	0.1	0.1568
			0.75	0.0242
			1	0.0182
	5	5	0.1	0.2319
			0.75	0.0387
			1	0.0293

Values of other thermodynamic parameters such as enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) can provide supplementary information about the mechanism of corrosion inhibition. The enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption on low carbon steel in hydrochloric acid in the presence of the inhibitors can be calculated by using the following equation [23]:

$$\ln K_{ads} = \ln\left(\frac{1}{55.5}\right) + \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \quad (8)$$

Using Eq. (8), the values of enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption were evaluated from the slope and intercept of the plot of $\ln K_{ads}$ versus $1/T$ (Fig. 7). The thermodynamic data of adsorption are depicted in Table 4. The values

obtained confirm the exothermic behavior of the adsorption process of PTU on the low carbon steel surface in hydrochloric acid. While an endothermic adsorption process ($\Delta H_{\text{ads}} > 0$) is attributed unequivocally to chemisorption, an exothermic adsorption process ($\Delta H_{\text{ads}} < 0$) may involve either physisorption or chemisorption or a mixture of both processes [24, 25].

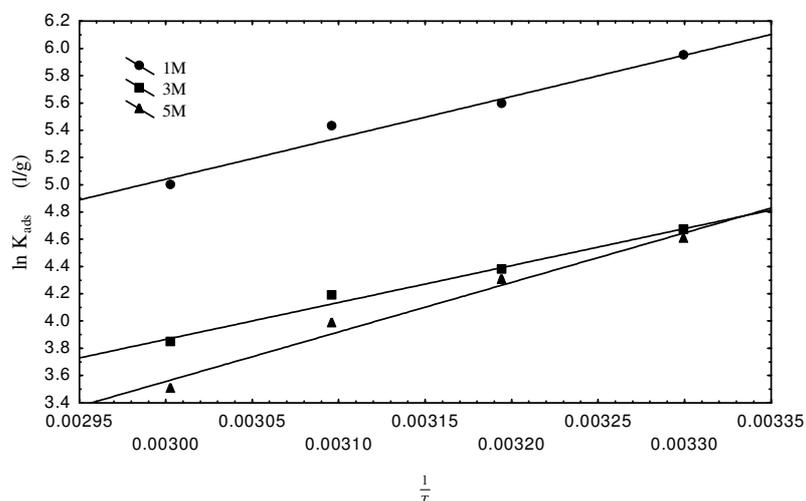


Figure 7. Plots of $\ln K_{\text{ads}}$ against $1/T$ for PTU on low carbon steel in 1, 3 and 5 M HCl.

In the present work, the negative value obtained may introduce physisorption processes which are confirmed by previous discussion. Also, the negative values of ΔH_{ads} show that the adsorption is exothermal with an ordered phenomenon ascribed by the negative values of ΔS_{ads} . This order may more probably be explained by the possibility of formation of iron complex on the metal surface [26, 27], or inhibitor molecules may freely move in the bulk of solution before the adsorption process, while with progress in adsorption the inhibitor molecules were orderly adsorbed on the metal surface, which resulted in the decrease in entropy [28].

Table 4. Thermodynamic parameters for adsorption of PTU on low carbon steel surface at different conditions.

HCl (M)	Temp (K)	K_{ads} (l/g)	slope	ΔG_{ads} (kJ.mol ⁻¹)	ΔH_{ads} (kJ.mol ⁻¹)	ΔS_{ads} (J.K ⁻¹ .mol ⁻¹)
1	303	383.753	0.987	-25.106	-13.085	-0.324
	313	267.201	1.055	-24.993		
	323	227.271	1.031	-25.357		
	333	148.413	1.026	-24.962		
3	303	106.697	1.062	-21.882	-22.533	-2.053
	313	79.838	1.040	-21.849		
	323	65.362	1.025	-22.010		
	333	46.511	1.016	-21.749		
5	303	99.484	1.075	-21.705	-30.214	-27.601
	313	73.699	1.052	-21.641		
	323	53.762	1.078	-21.485		
	333	33.115	1.090	-20.809		

Conclusion

The corrosion rate of steel increases with temperature in all acid concentrations in the presence and absence of the inhibitor. The variation of corrosion rate with temperature in 1, 3, and 5 M acid concentration obeys the Arrhenius equation adequately in absence of PTU as corrosion inhibitor. It is found that the activation energy decreases with increasing the acid concentration. Phenylthiourea is found to obey Langmuir adsorption isotherm expressed mathematically in all acid concentrations studied. Phenylthiourea is a very efficient inhibitor through out the studied regions of temperature and both acid and inhibitor concentrations, and it inhibits carbon steel from corroding by HCl by affecting both anodic and cathodic reactions, with the anodic reaction prevailing.

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