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Phenyl Thiourea as Corrosion Inhibitor for Mild Steel in Strong Hydrochloric Acid

Aprael S. Yaro and Dhuha A. Abdulaaima
Department of Chemical Engineering, College of Engineering, University of Baghdad, Iraq

Abstract

The inhibitive action of Phenyl Thiourea (PTU) on the corrosion of mild steel in strong Hydrochloric acid, HCl, has been investigated by weight loss and potentiostatic polarization. The effect of PTU concentration, HCl concentration, and temperature on corrosion rate of mild steel were verified using 2 levels factorial design and surface response analysis through weight loss approach, while the electrochemical measurements were used to study the behavior of mild steel in 5-7N HCl at temperatures 30, 40 and 50 °C, in absence and presence of PTU. It was verified that all variables and their interaction were statistically significant. The adsorption of (PTU) is found to obey the Langmuir adsorption isotherm. The effect of temperature on the adsorption process showed that the adsorption process is exothermic, spontaneous and represents mixed chemical and physical adsorption for PTU on the metal surface.

Key Words

Corrosion, Phenyl Thiourea, Electrochemical Measurements, dimensionless separation factor, Factorial Design, Adsorption, Activation parameters

Introduction

The corrosion of metals remains a world -wide scientific problem as it affects the metallurgical, chemical, and oil industries [1]. Hydrochloric acid is widely used for the removal of the rust and scale in several industrial operations [2]. When mild steel is used in these operations it suffers sever corrosion [3]. Using inhibitors is one of the most practical methods for protection against corrosion, especially in acid solutions, to prevent metal dissolution and acid consumption [4]. Organic compounds containing N and S have proved to be good inhibitors for the preventation of corrosion under acidic conditions [5]; therefore, thiourea and its derivatives have been extensively investigated as corrosion inhibitors in acidic media [6]. The main objective of this investigation is to study the inhibitive effect of Phenyl Thiourea (PTU) for the mild steel corrosion in strong hydrochloric acid using weight loss and potentiostatic methods.

Experimental Method

A mild steel sheet was used as working electrode of 20 mm (width), 30 mm (length) and 1 mm thickness in weight loss method. Area of (0.8 cm^2) was used for polarization method. Its composition is :(C=0.17-0.2, Mn<1.4, S<0.045, P< 0.045, Fe reminder). (5 and 7 N) Hydrochloric acid solutions were prepared using distilled water.

Weight Loss Method

The specimens were polished with emery papers and then cleaned with tap water, distilled water, benzene and acetone. After that they were dried and weighed on a digital scale. Each of the specimens is designated and its initial weight is noted. After each test, the specimen was washed with running tap water, scrubbed with a brush to remove corrosion products, then washed with tap water followed by distilled water and dried on clean tissue, immersed in benzene, dried, immersed in acetone, dried and left in a desiccators over silica gel for 1 hour before weighting. The time of immersion in HCl solutions was two hours.

Polarization Techneque

By using a Wenking M Lab potentiostat and a three electrode cell, electrochemical studies were performed. Platinum over Titanium (Pt/Ti) electrode was used as the auxiliary electrode and a saturated silver electrode Ag/AgCl as the reference electrode. The corrosion rates are determined by Tafel extrapolation technique. The experiments were conducted at 30, 40, and 50 °C.

Results and Discussions

Weight Loss Method

Table (1) represents the low and high levels factor, the matrix of the factorial design.

Table 1, Factors and levels used in 2^3 factorial design

variables	Low level (-1)	High level (+1)
Inhibitor concentration (ppm)	100	1000
Acid concentration (N)	5	7
Temperature (˚C)	30	70

Table (2) shows the experimental results.

Table 2, Effect of HCl concentration, PTU concentration, and temperature on corrosion rate of mild steel

No.	PTU (ppm) X_1	HCl (N) X_2	Temperature (˚C) X_3	Corrosion rate g/m².day
1	100	5	30	135
2	100	5	70	13970
3	100	7	30	1115
4	100	7	70	21874
5	1000	5	30	68
6	1000	5	70	1470
7	1000	7	30	254
8	1000	7	70	6173

Table (3) shows the main effects of the factors under study and their interaction on the corrosion rate of mild steel in HCl acid media in presence of phenyl thiourea (PTU).

Table 3, The variables effect and their interaction using PTU

Factor	Main effect or interaction
X_1	-7282.25
X_2	3443.25
X_3	10478.75
$X_1 X_2$	-998.75
$X_1 X_3$	-6818.25
$X_2 X_3$	2860.25

It is clear from Table (3) that the acid concentration and the temperature accelerate corrosion, and the effect of temperature is about 4 times larger than acid concentration. The inhibitor, on the other hand, decreases the corrosion rate sharply under the operating conditions. Yates method [7] was followed on the data which are given in Table (3). A mathematical expression to describe the design matrix combination mentioned in Table (2) as low and high level of each factor and its corresponding corrosion rates mentioned in Table (3) in code values were obtained as follows:

$$Y=5632.375-3641.125X_1+1721.625X_2+5239.375X_3+1430.125X_2X_3-499.375X_1X_2-3409.125X_1X_3 \quad \ldots(1)$$

Where: Y is the corrosion rate at each variable combination. X_1, X_2, X_3 are inhibitor concentration, acid concentration, and temperature, respectively. The results were analyzed using the analysis of variance (ANOVA) as appropriate to experimental design used. From ANOVA, the variables and their interaction effect on the corrosion rate were significant.

Polarization Technique

The polarization curves in the absence and the presence of PTU in (7 N HCl solutions) at different temperatures are presented in Figures 1 through 12, respectively. Table (4) shows the values of corrosion parameters obtained using Tafel extrapolation method.

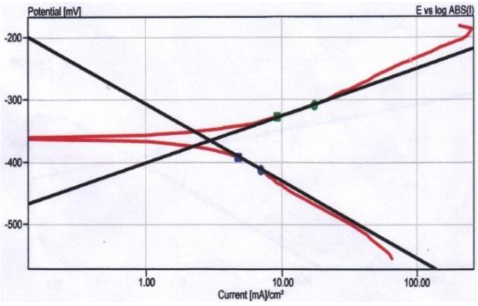

Fig.1, Polarization behavior of mild steel in 7N HCl in absence of PTU at temperature =30˚C

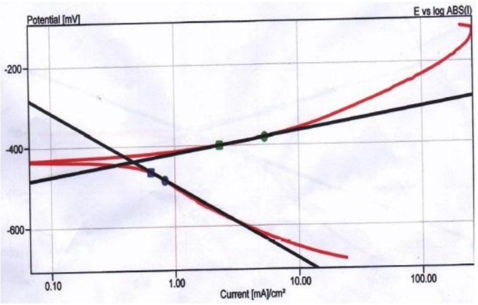

Fig.2, Polarization behavior of mild steel in 7N HCl in presence of 100 ppm of PTU at temperature =30˚C

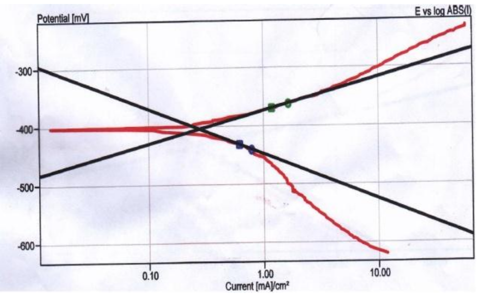

Fig. 3, Polarization behavior of mild steel in 7N HCl in presence of 550 ppm of PTU at temperature =30˚C

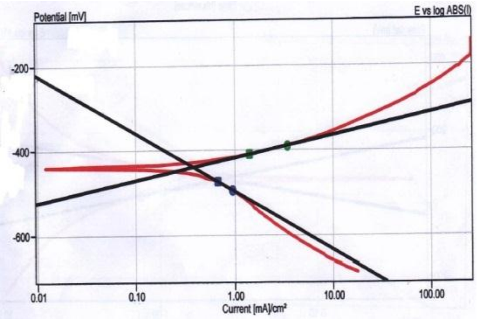

Fig. 4, Polarization behavior of mild steel in 7N HCl in presence of 1000 ppm of PTU at temperature =30˚ C

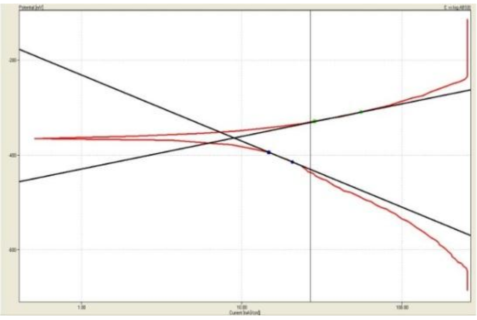

Fig. 5, Polarization behavior of mild steel in 7N HCl in absence of PTU at temperature =40˚C

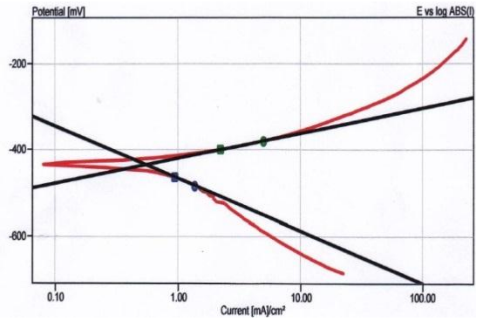

Fig. 6, Polarization behavior of mild steel in 7N HCl in presence of 100 ppm of PTU at temperature =40˚C

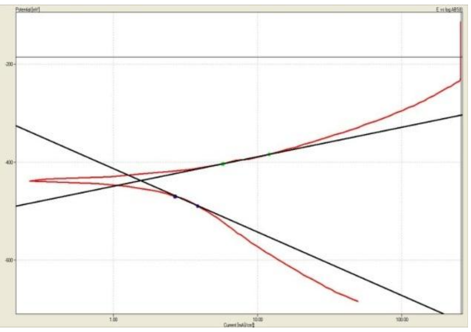

Fig. 7, Polarization behavior of mild steel in 7N HCl in presence of 550 ppm of PTU at temperature =40˚

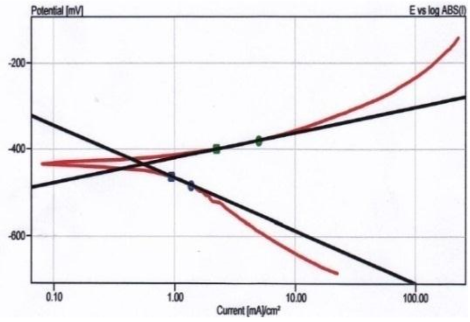

Fig. 8, Polarization behavior of mild steel in 7N HCl in presence of 1000 ppm of PTU at temperature =40˚ C

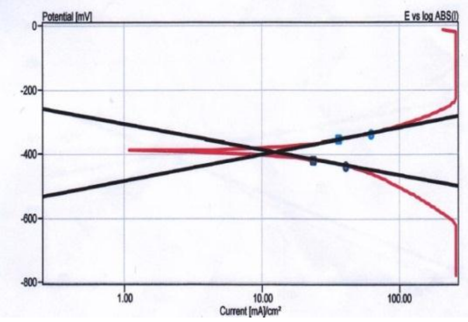

Fig. 9, Polarization behavior of mild steel in7N HCl in absence of PTU at temperature =50˚C

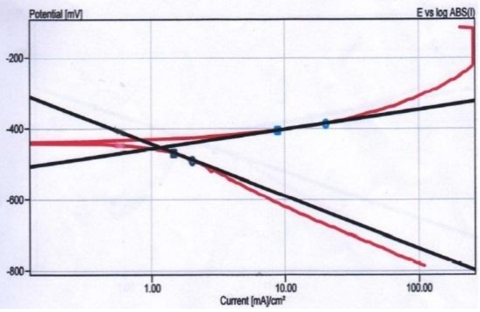

Fig. 10, Polarization behavior of mild steel in 7N HCl in presence of 100 ppm of PTU at temperature =50˚C

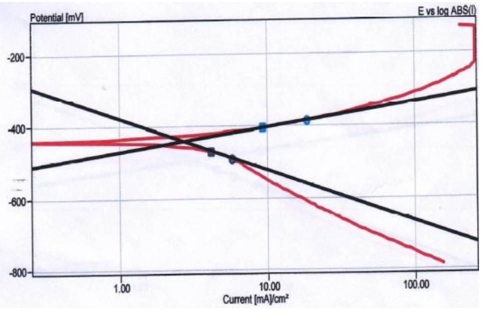

Fig. 11, Polarization behavior of mild steel in 7N HCl in presence of 550 ppm of PTU at temperature =50˚C

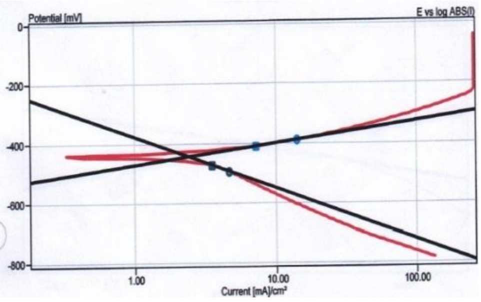

Fig. 12, Polarization behavior of mild steel in 7N HCl in presence of 1000 ppm of PTU at temperature = 50°C

Table 4, Corrosion parameters obtained for mild steel in 7N HCl at different temperatures and concentrations of PTU

PTU ppm	Temp K	E_{corr} mV	i_{corr} µA/cm²	b_a mV/dec	$-b_c$ mV/dec	IE (%)
Nil	303	-365	2380	76	124	......
	313	-364	7190	69	139	......
	323	-392	9840	83	79	......
100	303	-437	372	54	183	84.4
	313	-420	1440	74	106	80
	323	-453	935	55	147	90.5
550	303	-404	222	56	78	90.7
	313	-438	1240	60	129	82.8
	323	-441	2180	67	144	77.8
1000	303	-440	305	53	137	87.2
	313	-424	440	61	125	94
	323	-445	1940	72	173	80.3

Effect of Temperature and Activation Studies

Activation energy, $E_{act.}$, activation entropy, $\Delta S_{act.}$, and enthalpy of activation, $\Delta H_{act.}$ were calculated using Arrhenius equation:

$$\log i_{corr} = \log A - E_{act}/2.303\ RT \quad \ldots(2)$$

and its alternative formulation called transition state equation:

$$i_{corr} = (RT/Nh) \exp(\Delta S_{act.}/R) \exp(-\Delta H_{act.}/RT) \quad \ldots(3)$$

where, T is the absolute temperature, R, the universal gas constant, h is Planck´s constant, and N is Avogadro´s number.

From the corrosion current densities obtained from polarization curves at different temperatures in the absence and the presence of PTU as corrosion inhibitor, Arrhenius plots are shown in Figure 13 for a temperature range of (303-323 K) in 7N acid concentration. The activation energies calculated from Arrhenius plots, and the values of $\Delta S_{act.}$ and the $\Delta H_{act.}$ obtained from transition state plots with accepted regression coefficient are listed in table (5). Figure (14) shows transition state plots for temperature range of (303-323 K) in 7N acid concentration.

Table 5, Activation parameters for adsorption of PTU on mild steel at different conditions

PTU ppm	$E_{act.}$ kJ/mol	R^2	$\Delta H_{act.}$ kJ/mol	$\Delta S_{act.}$ J/mol. K	R^2
Nil	56.52	0.917	54.15	-0.919	0.914
100	56.59	0.938	54.26	-16.05	0.901
550	90.91	0.936	88.17	92.14	0.932
1000	72.63	0.873	70.08	32.21	o.867

From Table (5), it is observed that the activation energy, $E_{act.}$, and activation enthalpy, $\Delta H_{act.}$, 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 the positive sign for both $E_{act.}$ and $\Delta H_{act.}$, reflecting the endothermic nature of corrosion process [4]. The endothermic process is attributed to chemisorptions. All values of $E_{act.}$ are larger than the analogous values of ΔH_{act} indicating that the corrosion process must involve a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in total reaction volume [8].

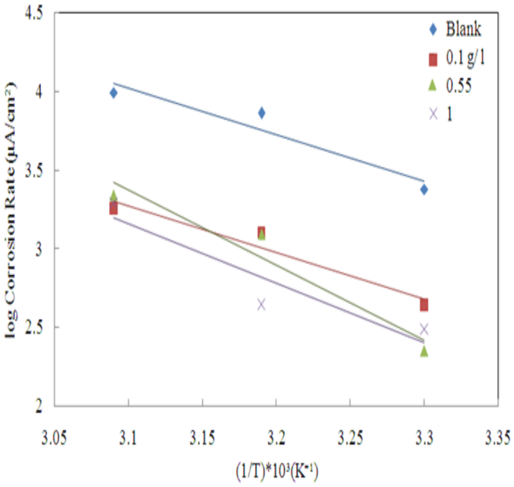

Fig.13, Arrhenius plot of mild steel in 7 N HCl contains different concentrations of PTU at different temperatures

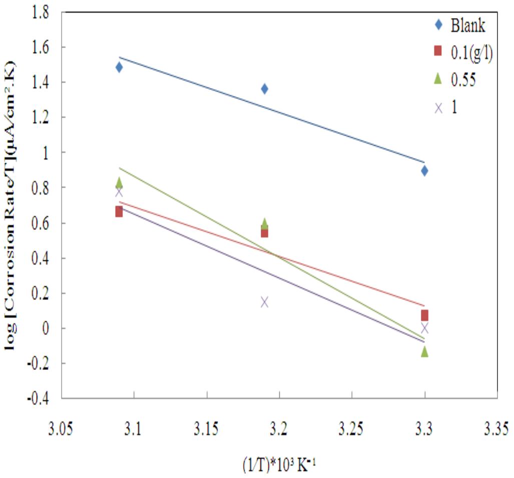

Fig.14, Transition state plot of mild steel in 7 N HCl contains different concentrations of PTU at different temperatures

The negative values of $\Delta S_{act.}$ 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 [9]. It means that a decrease in disordering take place on going from reactants to the activated complex [10, 11]. The increase of $\Delta S_{act.}$ reveals that an increase in disordering take place from reactant to activated complex [12].

Adsorption Isotherm Studies

Figure (15) shows the linear plots for C/ϴ versus C, suggesting that the adsorption obeys the Langmuire´s isotherm:

$$C/\Theta = 1/K_{ads} + C \qquad \ldots(4)$$

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 adsorped on the metal surface); the value of K_{ads} obtained from the reciprocal of intercept of Langmuir´s plot lines and the slop of these lines is near unity, which mean that each inhibitor molecule occupies one active site on the metal surface.

Moreover, the essential characteristic Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L [4], which describes the type of isotherm and is defined by:

$$R_L = \frac{1}{1 + K_{ads}\,C} \qquad \ldots(5)$$

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 (6) gives the estimated values of R_L for PTU in 7N HCl at different temperature. It was found that all R_L values are less than unity, confirming that the adsorption is favorable.

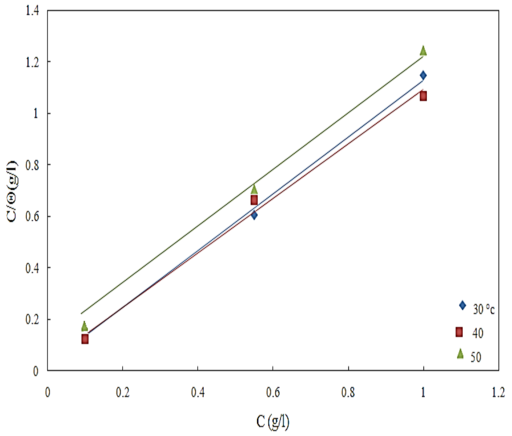

Fig.15, Langmuir adsorption isotherm of PTU on mild steel in7N HCl at different temperatures

The standard adsorption free energy ($\Delta G_{ads}°$) was calculated using the following equation [13]:

$$K_{ads} = (1/55.5)\exp(-\Delta G^{\circ}_{ads}/RT) \qquad \ldots(6)$$

Where, 55.5 is the concentration of water in solution expressed in molar, R is the gas constant, and T is the absolute temperature. The average value of standard adsorption free energy is ΔG_{ads}=-25.769 kJ/mol. 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 are consistent with electrostatic interaction between the charged molecule and the charged metal (physisorption), while those around -40 KJ/mol 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 [14]. 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 [15]. Therefore, for the present work the value of ΔG_{ads} is larger than the common physical adsorption values, but smaller than the common chemical adsorption values [16], probably meaning that both physical and chemical adsorption take place (i.e. comprehensive adsorption). The dependence of ΔG_{ads} on temperature can be explained by two cases as follows [17]:

1. ΔG_{ads} may increase (becomes less negative) with the increase in temperature which indicates the occurrence of exothermic process.
2. ΔG_{ads} may decrease (becomes more negative) with the increase in temperature which indicates the occurrence of endothermic process.

Table 6, Dimensionless separation factor R_L for PTU at various temperatures

Temp (K)	PTU (g/l)	R_L
303	0.1	0.218
	0.55	0.04
	1	0.027
313	0.1	0.253
	0.55	0.058
	1	0.0328
323	0.1	0.555
	0.55	0.185
	1	0.111

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 mild steel in hydrochloric acid in the presence of inhibitor can be calculated by using the following equation [18]:

$$\ln K_{ads} = \ln(1/55.5) + \Delta S_{ads}/R - \Delta H_{ads}/RT \quad \ldots(7)$$

Using equation (7), 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 as shown in Figure (16). The thermodynamic data of adsorption are depicted in Table (7).

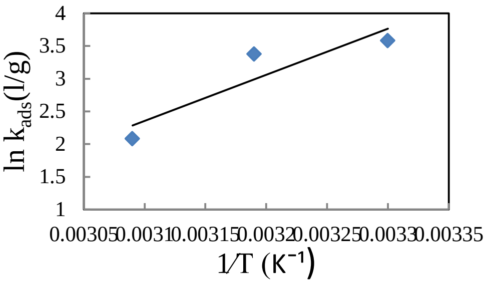

Fig.16, Plot of ln K_{ads} against 1/T for PTU on mild steel in 7N HCl at different temperatures

Table 7, Thermodynamic parameters for adsorption of PTU on mild steel surface in 7N HCl at different temperatures

Temp (K)	K_{ads} l/g	slope	ΔG_{ads} KJ/mol	ΔH_{ads} KJ/mol	ΔS_{ads} J/mol.K
303	35.71	1.100	-26.406	-58.74	-105.03
313	29.41	1.056	-26.773		
323	8	1.096	-24.13		

The values obtained confirm the exothermic behavior of the adsorption process of PTU on mild steel surface in hydrochloric acid. While an endothermic adsorption process (ΔH_{ads}>0) is attributed unequivocally to chemisorptions, an exothermic adsorption process (ΔH_{ads} <0) may involve either physisorption or chemisorption or a mixture of both processes [19, 20]. In the present work, the value obtained may introduce physisorption and chemisorption 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 [21, 22], 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[16].

Conclusions

1. Phenyl thiourea (PTU) represents effective inhibitor in 7N HCl at temperature range of 30 -50°C. The maximum inhibition efficiency was found to be 94% at 40°C and 1000 ppm of PTU.
2. The endothermic nature and chemisorption of corrosion process.
3. The adsorption of PTU is spontaneous and exothermic and follows Langmuir adsorption isotherm.
4. The adsorption of PTU is comprehensive (physical and chemical adsorption) for the inhibition process.

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References

1. A. O. James, N. C. Oforka, Olusegum K. Abiola, “Inhibition of acid corrosion of mild steel by Pyridoxal and Pyridoxal Hydrochloride”, Electrochem. Sci., 2(2007) 278-284.
2. G.Y. Elewady, “Pyrimidine Derivatives as Corrosion Inhibitors for Carbon-Steel in 2M Hydrochloric Acid Solution”, Electrochem. Sci., 3 (2008) 1149 – 1161.
3. P. Bothi Raja and M.G. Sethuraman, “Studies on the Inhibition of Mild Steel Corrosion by Rauvolfia serpentina in Acid Media” ,Journal of Materials Engineering and Performance, 19(5) 2010 761-766.
4. A. A. Khadom, A. S. Yaro, A. S. AlTaie, A. A. H. Kadum, “Electrochemical, Activations and Adsorption Studies for the Corrosion Inhibition of Low Carbon Steel in Acidic Media”, Port. Electrochem. Acta., 27(6),2009, 699-712.
5. Archana Gupta and M.M. Singh, “Inhibition of mild steel corrosion in formic acid by Thiourea, 2-Amino [4-p-Chloro Phenyl] Thiazole and different derivatives of their condensation products”, Port. Electrochem. Acta. 17 (1999) 21-43.
6. S.D.Setty,P.Shetty and H.V. S. Nayak, “Inhibition of mild steel in HCl acid by N-cyclohexyl-N-Phenyl thiourea”, Indian Journal of chemical technology,12(2005)462 465.
7. Davis, O. L., “Design and analysis of industrial experimentation”, Hafiner publishing Co. New York, N. Y. (1960).
8. E. A. Noor, “Temperature effect on corrosion inhibition of mild steel in acidic solution by aqueous extract of fenugreek leaves”, Electrochem. Sci., 2(2007) 996-1017.
9. E. A. Noor, “Evaluation of inhibitive action of some quaternary N heterocyclic compounds on the corrosion of Al–Cu alloy in hydrochloric acid”, Mater. Chem. Phys. 114 (2009) 533–541.
10. S. S. Abd El-Rehim, H. H. Hassan and M. A. Amin, “Corrosion inhibition of aluminum by 1,1(lauryl amido)propyl ammonium chloride in HCl solution”, Mater. Chem. Phys.70 (2001) 64-72.
11. G. K. Gomma and M. H. Wahdan, “Schiff bases as corrosion inhibitors for aluminum in hydrochloric acid solution”, Mater. Chem. Phys. 39 (1995) 209-213.
12. I. Naqvi , A. R. Saleemi, S. Naveed, “Cefixime: a drug as

efficient corrosion inhibitor for mild steel in acidic media electrochemical and thermodynamic Studies", Electrochem. Sci., 6 (2011) 146 – 161.

13. S.A. Umoren, E.E. Ebenso, "The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H_2SO_4", Mater. Chem. Phys., 106 (2007) 387-393.
14. S.A. Umoren, I.B. Obot, E.E. Ebenso, "Corrosion inhibition of aluminum using exudate gum from Pachylobus edulis in the presence of halide ions in HCl", E-journal Chem., 5 (2008) 355-364.
15. W.W. Damaskin, O.A. Pietrij, W.W. Batrakow, "Adsorption of organic compounds on electrode", Plenum Press", New York, 1971.
16. G. Mu, X. Li, G. Liu, "Synergistic inhibition between tween 60 and NaCl on the corrosion of cold rolled steel in 0.5 M sulfuric acid", Corros. Sci., 47(2005) 1932-1952.
17. L. Tang, G. Mu, G. Liu, "The effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 M hydrochloric acid", Corros. Sci., 45 (2003) 2251-2262.
18. B. A. Mohammed, K. N. Mohana, "The effect of sodium benzoate and sodium 4-(phenylamino) benzenesulfonate on the corrosion behavior of low carbon steel", Monatsh Chem/Chemical Monthly, 140 (2009) 1–8.
19. W. Durnie, R.D. Marco, A. Jefferson, B. Kinsella, "Development of a structure-activity relationship for oil field corrosion inhibitors", J. Electrochem. Soc., 146 (1999) 1751-1756.
20. S.A. Ali, A.M. El-Shareef, R.F. Al-Ghamdi, M.T. Saeed, " The isoxazolidines: the effects of steric factor and hydrophobic chain length on the corrosion inhibition of mild steel in acidic medium", Corros. Sci., 47 (2005) 2659-2678.
21. M. Abdallah and M.M. El-Naggar, "Cu+2 cation + 3, 5-dimethyl pyrazole mixture as a corrosion inhibitor for carbon steel in sulfuric acid solution", Mater. Chem. Phys., 71 (2001) 291-298.
22. A. Bousseksou, G. Molnár, J.A. Real, K. Tanaka, "Spin crossover and photomagnetism in dinuclear iron (II) compounds", Coord. Chem. Rev., 251 (2007) 1822-1833.