IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.8 No.1 (March 2007) 47-50

University of Baghdad
College of Engineering

Corrosion Inhibition of Low Carbon Steel in Different HCl Concentrations by Phenythiourea

Aprael S. Yaro*, Nashwan A. Rashed, and Ahmed S. Abdul-Hassan***

**Chemical Engineering Department - College of Engineering - University of Baghdad – Iraq*
***Chemical Studies Center – Ministry of Industry and Minerals - Iraq*

Abstract

Phenylthiourea (PHTU),was tested as inhibitor for the corrosion of low carbon steel in different HCl acid concentration by mass loss ,and polarization measurements .it was found that (PHTU) is a good inhibitor for the corrosion of low carbon steel in 1,3,and 5N HCl solution ,and its inhibition efficiency (θ) increases with its concentration and attains approximately 97% at 1g/l .polarization curves indicate that (PHTU) acts as an anodic type inhibitor .the inhibitor was adsorbed on the low carbon steel surface according to the Langmuir adsorption isotherm model. Results show that the rate of corrosion of low carbon steel increased with increasing temperature over the range 30-60°C, both in the presence of inhibitor and its absence .it was found also that the inhibiting effect of the inhibitor is generally acid concentration independent.

Keywords: phenylthiourea, low carbon steel, corrosion inhibition.

Introduction

To control the corrosion of metals in several industrial processes, acid inhibitors are usually used. Metals are exposed to the action of acids in many ways, and for many different reasons. The exposures can be most severe but in many cases, the corrosion can be controlled by means of inhibitors. Processes in which acids play a very important part are: Acids pickling, industrial acid cleaning and oil well acidizing [1]. Most of the well-known acid inhibitors are organic compounds containing nitrogen (N), such as amine and hetrocyclic compounds, besides sulphur and oxygen.

The influence of these organic inhibitors on the corrosion of steel in acidic solutions has been investigated by several workers [2-4].the existing data show, that most organic inhibitor used, act by adsorption on the metal surface .the selection of a suitable inhibitor for a certain process depends on many factors; such as: its chemical structural, its concentration, the nature of metal used and the type of acid used.

The aim of this study is to investigate the role played by phenylthiourea as corrosion inhibitor on the corrosion inhibition of low carbon steel in 1, 3, and 5 N HCl acid solutions.

Experimental Work

Gravimetric measurements

The experiments were carried out in solutions of uninhibited 1,3,&5N HCl acid solution on low carbon steel containing 0.041 %C ,0.311% Mg ,0.05% phosphorus,0.007% S, remainder% iron. Specimens in the form coupons with dimensions of (7.89x1.5) cm2 and a thickness of 0.09 cm were used for mass loss measurements studies. They were polished with emery paper of grad numbers 220,320,400 and 600, each run was carried out in a glass vessel containing 1000cm^3 test solution ,a clean weighed low carbon steel specimen was completely immersed in 1,3,&5 N HCl acid at 30,40,50,&60°C.After 2 hours of immersion in 1,3,&5N uninhibited HCl acid ,the specimen was drawn. Rinsed with distilled water, washed with ethanol& acetone, dried& weighted. The mass loss was used to calculate the corrosion rate in grams per meter square per day (gmd).

Polarization measurements

.Cylindrical electrode (1.96cm outside diameter and width of 0.5cm) ≈ 3.13 cm^2 area was prepared from investigated carbon steel. Samples were abraded in sequence under running tap water using emery paper of grad numbers 220,320,400 and 600 then washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, kept in a desicator over silica gel bed until use.

The concentration range of inhibitor used was:(0.1, 0.75, and 1 g/l).The studies were carried out potentiodynamically in a thermostated electricaltic cell .Platinum foil was used as a counter-electrode (CE)and a saturated calomel electrode as a reference electrode (SCE).The later was connected through a luggins capillary to the cell. The working electrode (WE) was immersed in a test solution .The potentiodynamic current-potential curves were recorded by changing the electrode potential manually from -800 to -100 mV (SCE).All experiments were carried out in freshly prepared solutions at constant temperatures :30, 40, 50, and 60°C.

Results and Discussion

Mass loss measurements

Table 1 collects the values of corrosion rate obtained from mass loss measurements for different temperatures in different HCl acid concentrations. Table 1 shows that corrosion rate of carbon steel is function of both the temperature &acid concentration .This means that for certain temperature or acid concentration, corrosion rate increases as the acid concentration or temperature increases respectively.

To elucidate or determine the activation energies of the corrosion process, mass loss measurements were preformed at various temperatures in the absence of inhibitor used.

It has been reported that, for iron &steel in acid, the logarithm of the corrosion rate of steel, CR, can be represented as a straight line function of (1/T) (Arrhenius equation):

$$\log CR = -\frac{E}{2.3RT} + B \qquad (1)$$

Where E is the activation energy, R, is the universal gas constant and B is a constant. The variation in logarithm of corrosion rate of carbon steel in 1, 3, and 5N HCl acid solutions in the absence of inhibitor, with reciprocal of the absolute temperature, is given in Fig 1.The calculated value of (E), shows that increasing of acid concentration from 1N to 5 N was associated with a decrease in activation energy from 16 to 12.5 Kcal/mol respectively through 13.7 Kcal/mol in 3N HCl acid.

Several values given in the literature for activation energy of carbon steel in HCl solutions, ranging from 13.8 to 21.0 Kcal/mol [5], with majority grouped at about 14.5 Kcal/mole. Yaro [6] obtained a value of 14.26 Kcal/mole for the corrosion of carbon steel in 1N HCl acid solution.

Electrochemical measurements

Potentiodynamic anodic and cathodic polarization scans were carried out at 30, 40, 50, and 60 °C in 1, 3, and 5N HCl with different concentrations of (PHTU). Anodic and cathodic polarization curves in absence and in the presence of inhibitor at different concentrations after immersion in 1, 3, and 5 N HCl acid solution at 30°C are shown in Fig. 2-4 as a sample (i.e., the polarization curves at 40, 50, and 60°C at different inhibitor concentration immersed in 1, 3, and 5 N are not shown here, but they were used to find corrosion parameters i_{corr}, $ß_a$, and $ß_c$).

It can be seen from Figures 2-4, that in the presence of inhibitor, the curves are shifted to lower current regions, showing the inhibition tendency of (PHTU). The values of various electrochemical corrosion parameters are summarized in Table 2.

The E_{corr} values were generally shifted pronounsly in the presence of inhibitor to the positive direction. These observations show clearly that the inhibition of corrosion is under anodic control (i.e., polarization occurs on the anodic & the E_{corr} shifted to the open circuit of the cathode) [7].

The corrosion current densities and Tafel slopes were estimated by BETACRUNCH program developed by Green and Gandi [8] on the assumption that the corrosion reaction is completely under activation control and is not complicated with IR drop or mass transfer. Inhibition efficiency was then calculated using the mathematical expression:

$$\theta = \left(1 - \frac{IcorrIn}{IcorrUn}\right) \qquad (2)$$

Where $I_{corr.}$ (In) and $I_{corr.}$(un) are the corrosive current with and without inhibitor receptively.

Table 2 shows that an increase in inhibition in inhibitor concentration is resulted in increased inhibition efficiency, it is evident from the results that the i_{corr} values considerably decreased in the presence of inhibitor and that the maximum decrease in i_{corr} coincides with the maximum concentration of inhibitor [9] .the inhibitor studied performed excellently (96.5% inhibition efficiency at 1g/l) as inhibitor of the corrosion of low carbon steel in 1N HCl.

Surface coverage (θ) values have been evaluated for different concentration of (PHTU) under study from corrosion rates in uninhibited and inhibited solutions using Eq. 2. The Langmuir adsorption isotherm expressed as:

$$\theta = \frac{KC}{1+KC} \qquad (3)$$

Where K is the equilibrium constant for the adsorption isotherm process, C is the inhibitor concentration (g/l) and θ is the surface coverage. Rearranging Eq. 3:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (4)$$

It was found that Fig. 5 (plots of C/θ vs. C) for phenylthiourea inhibitor gives straight lines with slope, practically equal to unity, indicating that the adsorption of PHTU under consideration on carbon steel in 1, 3, and 5N HCl acid solutions interface obeys Langmuirs adsorption isotherm. It is important to mention here that the same behavior was obtained at 40, 50, and 60°C.

The deviation of the slope from unity is attributed to the difference in the rate of interaction between the adsorbed species on the metal surface.

From the intercept of the straight lines on the C/θ axis, K values were calculated. Table 3 shows the equilibrium constant for Langmuir type adsorption of PHTU inhibitor in 1N HCl acid solution at different temperature.

Table 1 effect of temperature and HCl acid concentration on the corrosion rate (g/m^{2}day) of carbon steel

HCl Conc.	Temperature, °C 30°C	40°C	50°C	60°C
1N	39.35	153.82	279.81	456.17
3N	75.85	177.82	741.31	1905.46
5N	602.55	1318.25	2454.71	3990.249

Table 2 Corrosion Current density, ßa, ßc and Eff. values obtained for Low Carbon Steel in different acid concentrations in absence &presence of PHTU

Run No.	Condition	I_{corr} µA/cm^2	β_c mV/dec	β_a mV/dec	Eff. %
	30°C:1N HCl				
1	Nil	315.71	55.73	63.91	Nil
2	0.1g inh.	21.19	40.83	50.85	93.2
3	075g inh.	17.22	44.94	53.29	94.54
4	1g inh.	14.93	46.93	65.56	95.27
	30°C:3N HCl				
5	Nil	641.89	49.25	51.78	Nil
6	0.1g inh.	91.55	47.66	51.25	85.73
7	0.75g inh.	51.46	50.82	34.02	91.98
8	1g inh.	46.5	42.07	46.62	92.75
	30°C:5N HCl				
9	Nil	757.31	40.38	42.38	Nil
10	0.1g inh.	125.05	42.25	45.77	83.48
11	0.75g inh.	84.22	40.53	43.09	88.87
12	1g inh.	70.69	42.44	45.69	90.66
	40°C:1N HCl				
13	Nil	1033.89	53.08	54.11	Nil
14	0.1g inh.	65.98	47.17	61.71	93.61
15	0.75g inh.	50.19	73.68	83.67	95.14
16	1g inh.	42.93	44.28	52.57	94.84
	40°C:3N HCl				
17	Nil	1211.33	70.95	71.55	Nil
18	0.1g inh.	111.34	39.14	43.04	90.8
19	0.75g inh.	85.65	40.82	47.19	92.9
20	1g inh.	67.03	48.73	56.89	94.4
	40°C:5N HCl				
21	Nil	3178.36	70.95	71.55	Nil
22	0.1g inh.	399.23	101.47	118.83	87.43
23	0.75g inh.	289.9	88.74	99.08	90.87
24	1g inh.	229.39	85.9	92.6	92.78
	50°C:1N HCl				
25	Nil	1601.07	46.74	47.54	Nil
26	0.1g inh.	111.71	43.57	49.28	93.02
27	0.75g inh.	64.84	41.74	49.16	95.96
28	1g inh.	58.77	48.22	56.16	96.32
	50°C:3N HCl				
29	Nil	6199.28	95.97	97.99	Nil
30	0.1g inh.	903.89	46.76	48.47	85.41
31	0.75g inh.	576.15	46.09	50.92	90.7
32	1g inh.	379	43.64	46.32	93.88
	50°C:5N HCl				
33	Nil	9987.17	104.67	105.89	Nil
34	0.1g inh.	2022.95	52.21	52.71	79.7
35	0.75g inh.	1576.41	48.71	53.95	84.2
36	1g inh.	1182.42	49.62	51.85	88.16
	60°C:1N HCl				
37	Nil	2594.68	52.62	53.05	Nil
38	0.1g inh.	199.35	63.83	74.64	92.31
39	0.75g inh.	109.24	33.41	34.09	95.78
40	1g inh.	92.3	43.01	49.69	96.44
	60°C:3N HCl				
41	Nil	5996.51	67.51	69.11	Nil
42	0.1g inh.	1088.58	35.11	35.43	81.84
43	0.75g inh.	876.04	46.43	51.64	85.39
44	1g inh.	527	38.18	42.92	91.21
	60°C:5N HCl				
41	Nil	10454.98	78.57	79.13	Nil
42	0.1g inh.	1840.71	47.58	48.17	77.48
43	0.75g inh.	1622.14	61.78	73.83	82.39
44	1g inh.	1354.15	48.19	49.17	84.48

Table 3 Equilibrium Constant for Langmuir Type Adsorption of the PHTU inhibitor in 1N HCl acid solution at Different Temperatures

Temperature(°C)	*K Value* (g/l)$^{-1}$	*Slope*
30	7.92	0.987
40	8.21	1.055
50	8.9	1.031
60	9.4	1.026

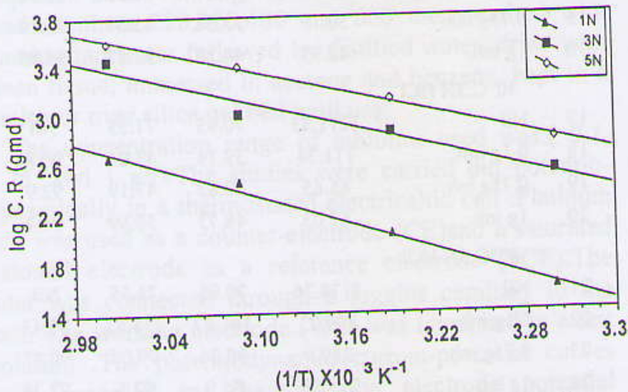

Fig. 1 Arrhenius plot for log corrosion rates (gmd) vs. reciprocal of absolute temp. at different HCl acid conc.

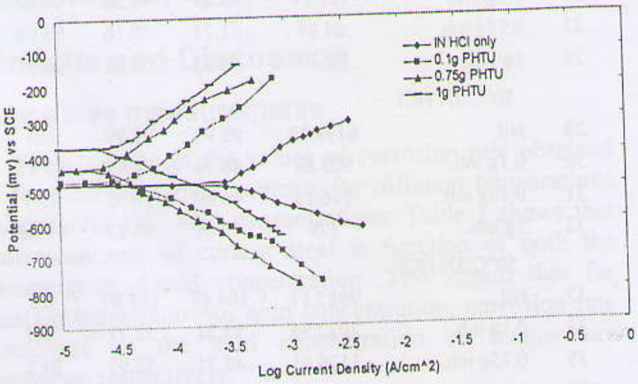

Fig. 2 Polarization curves of low carbon steel in 1N HCl containing different inhibitor concentration at 30°C

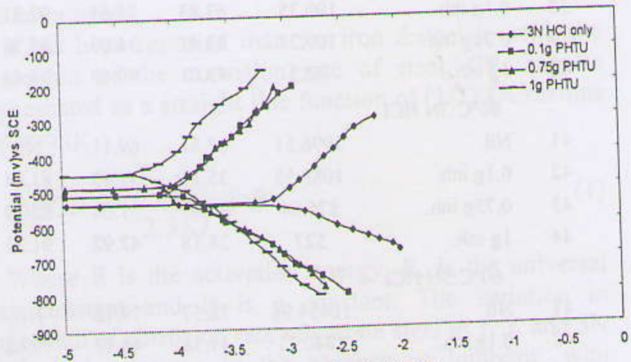

Fig. 3 Polarization curves of low carbon steel in 3N HCl containing different inhibitor concentration at 30°C

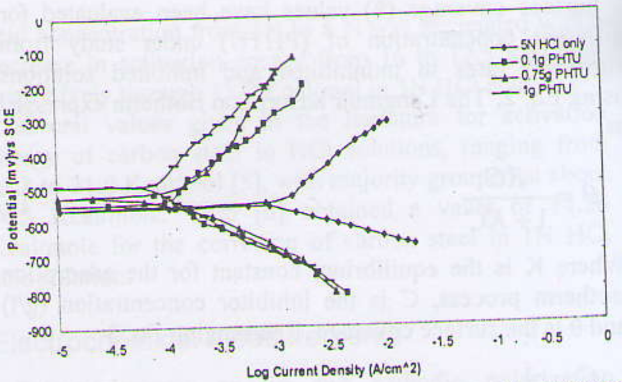

Fig. 4 Polarization curves of low carbon steel in 5N HCl containing different inhibitor concentration at 30°C.

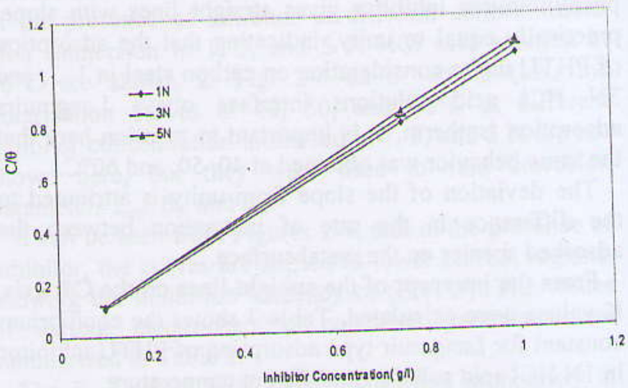

Fig. 5 Langmuir adsorption isotherm of PHTU on low carbon steel in different normality of HCl acid solution at 30°C.

References

1. G. George, Corrosion Inhibitor, NACE, Houston, Taxes, (1974).
2. J.M.Syker, Br.corros. J.25, 175 (1990).
3. M. Ajmal, A.S. Mideen, M.A. Quraiski, Corros.Sci., 36, 79 (1994).
4. M. Elachouri et al, Corros. Sci., 37, 381 (1995)
5. O.Riggs, JR. and R.Hurd, Corrosion, vol.23, 8, (1967).
6. A.S.Yaro, M.Sc. Thesis, University of Baghdad Jun.(1987).
7. AL-Amiry, M., M.Sc. Thesis, University of Baghdad (1989).
8. N. Green, and R. Gandi, Material Performance, July (1982).
9. AL-Saaty, H., M.Sc. Thesis University of Baghda (1988).