

## THE EFFECT OF TEMPERATURE AND ACID CONCENTRATION ON POLARIZATION RESISTANCE FOR A CORROSION REACTION UNDER ACTIVATION CONTROL

Aprael Sarguis Yaro

Chemical Engineering Department, College of Engineering, University of Baghdad

### ABSTRACT

The effect of temperature (30,40,50, and 60°C) on the polarization resistance ( $R_p$ ) has been analyzed for the corrosion of carbon steel in 1,3, and 5N HCl solution in absence & presence of phenylthiourea (PHTU) as corrosion inhibitor. The polarization resistance was measured at above mentioned conditions using BETACRUNCH program developed by Green and Gandi [Green, 1982]. i.e; Values of applied current densities at potentials of +20,+10,-10 mv and then -20,+10,-10mV(SCE) from corrosion potentials were used to obtain corrosion parameters:  $i_{Corr}$ ,  $b_a$ ,  $b_c$  followed by applying the equation:  $R_p = (b_a b_c) / 2.303 \times i_{Corr} (b_a + b_c)$ . It is observed that: (i) for a certain acid concentration the polarization resistance decreased with increase in temperature and/or decrease in inhibitor concentration. (ii) for a certain temperature, the polarization resistance decreases with an increase in acid concentration in presence and absence of inhibitor.

### KEY WORDS

Inhibition, polarization resistance Betacrunch program, physical adsorption, Chemical adsorption, activation control.

### الخلاصة

تم في هذا البحث تحليل تأثير درجة الحرارة (30,40,50, و60 درجة مئوية) على مقاومة الاستقطاب لعملية تآكل الحديد في ثلاث تراكيز مختلفة من حامض الهيدروكلوريك (5 و31 عيارى) بوجود و عدم وجود فينايل ثايو يوريا كمثبط لعملية التآكل (من منحنيات مقاومة الاستقطاب تم قياسها ضمن الظروف المذكورة باستعمال برنامج (بيتاكرانج) والتي طوره كرين و غاندى (من منحنيات الاستقطاب التي تم الحصول عليها للظروف المذكورة تؤخذ قيم لكثافة التيارات المسلطة في جهود +20, +10, -10 مللي فولت و -20, +10, -10 مللي فولت بعدا من جهد التآكل) باستعمال هذه الجهود مع كثافة التيارات المقابلة لها سيقوم البرنامج بايجاد متغيرات التآكل وبالتحديد تيارات التآكل و منحنيات تافل الموجبة و السالبة بطريقة التكرار وصولا الى اقل نسبة خطأ (تعووض متغيرات التآكل في معادلة الاستقطاب الخطى المعروفة للحصول على مقاومة الاستقطاب) عند تحليل النتائج لوحظ ان: (1) لتركيز حامض معين تقل مقاومة الاستقطاب بزيادة درجة الحرارة وتقليل تركيز المثبط (2) لدرجة حرارة معينة, مقاومة الاسقطاب تقل بزيادة تركيز الحامض بوجود و عدم وجود المثبط

### INTRODUCTION & THEORY

The polarization resistance is a measure of the resistance of a metal undergo corrosion in a certain environment. It is defined as the slope of the potential-current (E-i) curve

$$R_p = [\partial E / \partial i]_{E=E_{Corr}} \quad (1)$$

where  $i$ , is the current density in  $A/cm^2$  and  $E_{Corr}$  is the electrode potential of the corroding metal. Polarization resistance behave like a resistor and can be calculated by taking the inverse of the slope of the current –potential curve at open circuit corrosion potential. During the polarization

of an electrode, the magnitude of the current is controlled by reaction kinetics and diffusion of reactants both toward and away from the electrode. The Butler- Volmer equation is introduced in this case as[Stern,1957]:

$$i = i_{\text{Corr.}} [\exp(2.3 \Delta E / b_a) - \exp(-2.3 \Delta E / b_c)] \quad (2)$$

Where  $\Delta E = E - E_{\text{Corr.}}$ ,  $b_a$ ,  $b_c$  are anodic and cathodic Tafel constants. Equation (2) for small  $\Delta E$ , i.e; less than 20 mV from  $E_{\text{Corr.}}$ , can be linearized leading to:

$$i = i_{\text{Corr.}} [1 + 2.3 \Delta E / b_a - (1 - 2.3 \Delta E / b_c)] \quad (3)$$

$$i = i_{\text{Corr.}} [1 + 2.3 \Delta E / b_a - 1 + 2.3 \Delta E / b_c] \quad (4)$$

So, 
$$i = i_{\text{Corr.}} [2.3 \Delta E (1 / b_a + 1 / b_c)] \quad (5)$$

Rearranging equation (5) leads to:

$$\Delta E / i = R_p = (b_a b_c) / 2.3 i_{\text{Corr.}} (b_a + b_c) \quad (6)$$

Equation (6) is essentially the original Stern- Geary equation expressed in Tafel slopes of both reaction:  $\text{Fe} \longrightarrow \text{Fe}^{+2} + 2e$  (7)



(i.e;the effect of dissolved oxygen concentration is negligible compared with  $\text{H}_2$  evolution).Substituting in equation (6) for  $b_a$  and  $b_c$  as:  $b_a = RT / \alpha_a z_a F$ ;  $b_c = RT / \alpha_c z_c F$  (9)

Equation (6) can be expressed in terms of  $T, \alpha_a, \alpha_c, z_a, z_c$

$$R_p = RT / 2.3 \times i_{\text{Corr.}} F (\alpha_a z_a + \alpha_c z_c) \quad (10)$$

Equation (10) can be rearranged and put in Logarithmic form :

$$\text{Log}(R_p / T) = - \text{Log}(i_{\text{Corr.}}) + \text{Log}[R / 2.3 F (\alpha_a z_a + \alpha_c z_c)] \quad (11)$$

Accordingly, a Logarithmic plot of  $(R_p / T)$  V'S  $i_{\text{Corr.}}$ , gives a straight line with a slope of (-unity) provided  $(\alpha_a z_a)$  and  $(\alpha_c z_c)$  are constant. The polarization resistance has been used in corrosion monitoring [Neufeld,1964 & Tamba,1982], determination of corrosion rates [Mahmoud,2005 & Mishra,2007] and inhibitor efficiency[Ashassi,2006].The literature has few references to systematic measurements of the effect of temperature on the polararization resistance and few to a theoretical analysis of this effect[El-Anadouli,1986].But no references to the effect of acid concentration.This is the object of this paper.We have measured the polarization resistance of carbon steel corrosion in three different concentrations of HCl acid,namely, 1,3,and 5N acid solutions at various temperatures in presence of different concentrations of phenylthiourea(PHTU) as corrosion inhibitor using a well-known technique in corrosion field and away from  $E_{\text{Corr.}}$  by 20 mV for each condition studied, rather than the plot of potential,E,V'S current density,i,which leads to slopes of straight lines(i,e; $R_p = \Delta E / \Delta i$  at  $E = E_{\text{Corr.}}$ ).

## EXPERIMENTAL METHODE

Details of the polarization cell,electrode and electrolyte preparation and experimental techniques are reported elsewhere[Abdul-Hassan,2004]. The electrode was prepared from a carbon steel pipe as cylindrical specimens of chemical composition: Wt.%, C= .041, Mg =,381, P =.05, S = .007,remainder iron. The electrolyte was 1,3, and 5N HCl acid solutions prepared from distilled water and concentrated HCl acid supplied by Al- Furat company for chemical industries: The specifications of acid were as follows:Concentration = 32% Wt.,  $\text{SO}_4^{-2} = 125.5$  ppm, residue = 360 ppm and density =  $1.164 \text{ gm/Cm}^3$ . The inhibitor used was phenylthiourea (PHTU) of annular grade, MW =152.2 gm/mole, while acetone and benzene were used for cleaning purposes.

## RESULTS & DISCUSSION

From the polarization curves which represent the plots of potential,E, V's Log(current density),i, for the working electrode at different temperatures and in various acid concentrations in absence and presence of PHTU as corrosion inhibitor[Abdul-Hassan,2004], and from the average values of



corrosion parameters:  $i_{\text{Corr.}}$ ,  $b_a$ ,  $b_c$  obtained by applying the Betacrunch program by entering two sets of data for each condition as mentioned before. The values of  $R_p$  are deduced for the working electrode. These values for the working electrode for each condition are listed in Tables (1) through (4).

**Table 1 Polarization resistance( $\Omega\text{cm}^2$ ) of carbon steel in different concentrations of HCl acid containing various concentrations of PHTU as corrosion inhibitor at 30<sup>0</sup>C.**

Inhibitor Conc.(Mole/L)	1N	3N	5N
Nil	40.95	17.1	11.8
$6.6 \times 10^{-4}$ M	464.1	117.3	76.4
$4.9 \times 10^{-3}$ M	614.8	172.3	107
$6.6 \times 10^{-3}$ M	792.1	207.4	135

**Table 2 Polarization resistance( $\Omega\text{cm}^2$ ) of carbon steel in different concentrations of HCl acid containing various concentrations of PHTU as corrosion inhibitor at 40<sup>0</sup>C**

Inhibitor Conc.(Mole/L)	1N	3N	5N
Nil	11.3	12.8	4.9
$6.6 \times 10^{-4}$ M	175.5	79.9	59.3
$4.9 \times 10^{-3}$ M	339	111.2	70.3
$6.6 \times 10^{-3}$ M	243.2	171	84.7

**Table 3 Polarization resistance( $\Omega\text{cm}^2$ ) of carbon steel in different concentrations of HCl acid containing various concentrations of PHTU as corrosion inhibitor at 50<sup>0</sup>C**

Inhibitor Conc.(Mole/L)	1N	3N	5N
Nil	6.4	3.4	2.3
$6.6 \times 10^{-4}$ M	90	11.4	5.64
$4.9 \times 10^{-3}$ M	151.2	17.2	7.1
$6.6 \times 10^{-3}$ M	191.6	25.8	9.4

**Table 4 polarization resistance( $\Omega\text{cm}^2$ ) of carbon steel in different concentrations of HCl acid containing various concentrations of PHTU as corrosion inhibitor at 60<sup>0</sup>C.**

Inhibitor Conc.(Mole/L)	1N	3N	5N
Nil	4.4	2.5	1.64
$6.6 \times 10^{-4}$ M	75	7	5.7
$4.9 \times 10^{-3}$ M	67	12.1	9
$6.6 \times 10^{-3}$ M	108.9	16.6	7.6

At different temperatures and various acid concentration, also,  $\Theta$ , and I%, can be determined from  $R_p$ , obtained by using the following equations, respectively:

$$\Theta = 1 - (R_p)_{\text{free}} / (R_p)_{\text{inhib.}} \quad (12)$$

$$I\% = [ 1 - (R_p)_{\text{free}} / (R_p)_{\text{inhib.}} ] \times 100 \quad (13)$$

where  $(R_p)_{\text{free}}$  &  $(R_p)_{\text{inhib.}}$  are polarization resistance in absence and presence of inhibitor, respectively, while  $\Theta$  & I% are surface coverage and inhibition efficiency respectively. Table(5) shows the inhibition efficiency of PHTU under the operating conditions mentioned previously.

**Table 5 Inhibition efficiency of PHTU for carbon steel in different HCl acid concentrations and various temperatures.**

Temp Acid Conc.	30 <sup>0</sup> C			40 <sup>0</sup> C			50 <sup>0</sup> C			60 <sup>0</sup> C		
	1N	3N	5N	1N	3N	5N	1N	3N	5N	1N	3N	5N
.00066M	91.2	85.5	84.6	93.6	84.0	91.8	93.0	70.2	59.2	94.1	65	71
.0049M	93.3	90.1	89.0	96.7	88.4	93.0	96.0	80.2	67.5	93.4	80	82
.0066M	94.8	91.8	91.3	95.4	92.5	94.2	97.0	87.0	75.5	96.0	85	78
Inhibition Efficiency (I%) at different Temperatures & acid Concentrations												

Figures(1) through (3) show the effect of temperature and inhibitor concentration on the polarization resistance at acid concentrations 1,3,and 5N respectively. It is clear that polarization resistance decreases as the temperature increases and / or the inhibitor concentration decreases. The effect of inhibitor is clearly evident from equation(10). Thus, at constant temperature the increase in inhibitor concentration decreases the corrosion rate,  $i_{\text{Corr.}}$ , and hence,  $R_p$ , increases. ( i.e; the corrosion reaction is regarded as a rate process, the rate of which is given by [Potilova,1960] :

$$i_{\text{Corr.}} = A \exp(- E / RT) \quad (14)$$

Thus, as T increases the numerator increases linearly, while the denominator increases exponentially, and hence  $R_p$  decreases. The Logarithmic form of equation (10) is given in equation (11), from which a Logarithmic plot of  $( R_p / T )$  V's  $i_{\text{Corr.}}$  gives a straight line with a slope of [-unity], provided  $\alpha_a Z_a$  and  $\alpha_c Z_c$  are constants. Figures (4) through (6) show such plot at various temperatures and inhibitor concentrations in HCl acid concentrations 1 ,3, and 5N respectively. The straight lines are the least squares correlation of all the data points at 1,3, & 5N HCL acid, with a correlation coefficient of (.98) and slopes of ( 1.042 ) , ( 1.04 3 ) , and(.98 ) respectively,

In satisfactory agreement with the prediction of equation (11). These are taken as confirmation of the validity of this equation, and of constancy of  $\alpha_a Z_a$  and  $\alpha_c Z_c$  at various temperatures and inhibitor concentrations within the limits of experimental error. Combination of equation (14) and (11) leads to:

$$\text{Log} (R_p / T) = E / 2.3 R T + \text{Constant} \quad (15)$$

where the constant in equation (15) includes  $A, R, F, \alpha_a Z_a$ , and  $\alpha_c Z_c$ . Thus a plot of  $\text{Log}(R_p / T)$  V's  $1/T$  gives a straight line from the slope of which, Activation energy of the corrosion process can be calculated. Figures (7) through (9), illustrate such plots at various concentrations of PHTU in different HCl acid concentrations. The relation between  $\text{Log}(R_p / T)$  and  $1/T$  is satisfactory straight line under all conditions in agreement with equation (15). Table(6) lists the values of Activation energy obtained in the absence and presence of various inhibitor concentrations of PHTU in different acid concentrations. Since only small differences are observed between the values of activation energy calculated at different concentrations of the same inhibitor in 1N HCl acid, the activation energy is considered to be essentially independent of inhibitor concentration and in this case the inhibitor is physically adsorbed on the mild steel [Ebenso,1998 & Demaskin,1971]. i.e; when the activation energy is less than 80 kJ/mole, the adsorption is considered to be physically. Ideally, a corrosion inhibitor is a substance which greatly increases the activation energy of corrosion and / or adsorbs on the surface and prevents it from corroding. PHTU as corrosion inhibitor increases activation energy pronoucnly in 3 and 5N HCl acid solutions and hence the mechanism of its inhibition must not be via simple blocking adsorption. The large values of activation energy in both 3 and 5N acid solutions compared with 1N-HCl system support the fact that PHTU in this case is chemically adsorbed. i.e; Activation energy > 80 KJ/mole [Abiola,2002 & Barrow,1983].

**Table 6 Activation energies of corrosion of carbon steel at various concentrations of PHTU in different concentrations of HCl acid.**

Inhibitor Conc.(M/L)	1N	3N	5N
	E (kJ Mole)	E (kJ / Mole)	E (kJ / Mole )
Blank	63.0	61.8	58.2
.00066 M	59.3	84.1	87.1
.0049 M	64.8	89.4	83.7
.0066 M	54.6	81.6	92.7
$E_{\text{mean inhibited}}$	57.8	85.0	87.8

It is important to mention that Betacrunch program [Green,1982] is usually used to obtain the corrosion parameters near the corrosion potential by about +20 to -20 mV. Since the equation(6) derives with out assumptions and its derivation is completely mathematical, and since Tafel slopes are difficult to estimate. Moreover since the corrosion potential in this study especially at these high concentrations of HCL acid is not near the reversible potentials of one of the half reactions (i.e; The  $H_2$  evolution or the metal dissolution). It is accepted to say:  $R_p = f( i_{\text{corr}}, b_a, b_c )$  all at  $E = E_{\text{corr}}$ . instead of using the reciprocal of the polarization resistance obtained experimentally to represent the corrosion rate for screening purposes:  $i_{\text{cor}} = f( R_p, B )$ .

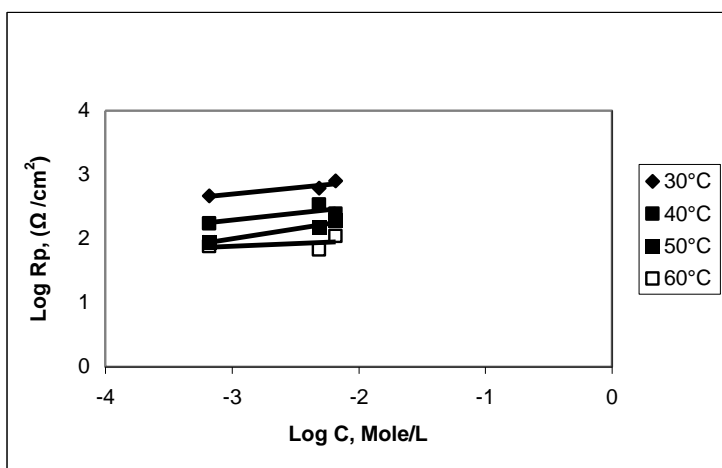


Fig.1 Effect of Temperature and inhibitor concentration on the polarization resistance in 1N HCL acid

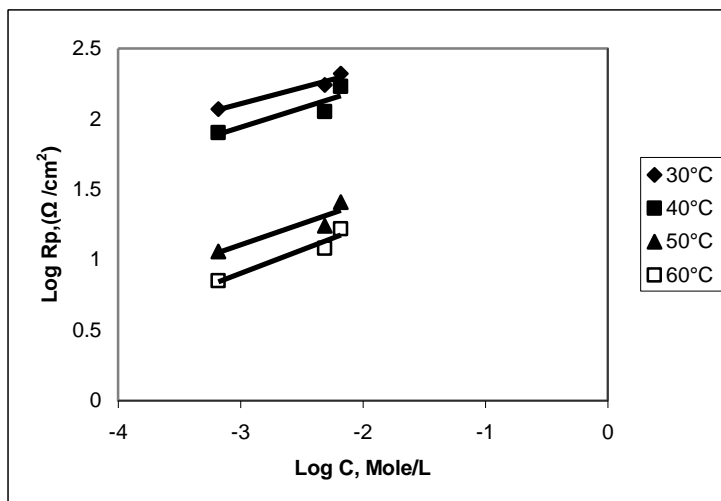


Fig.2 Effect of Temperature and inhibitor concentration on the polarization resistance in 3N HCL acid

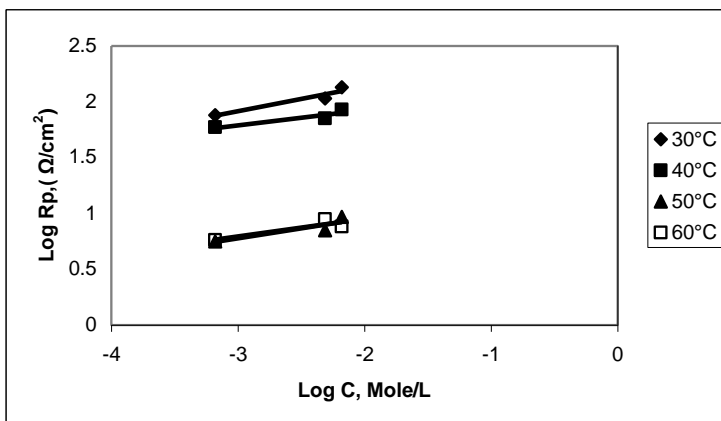


Fig.3 Effect of Temperature and inhibitor concentration on the polarization resistance in 5N HCL acid.

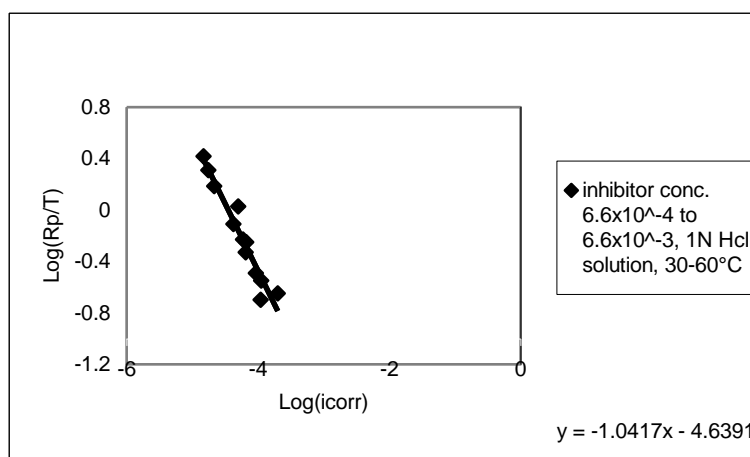


Fig. 4 Plot of polarization resistance data in 1N HCl acid solution.

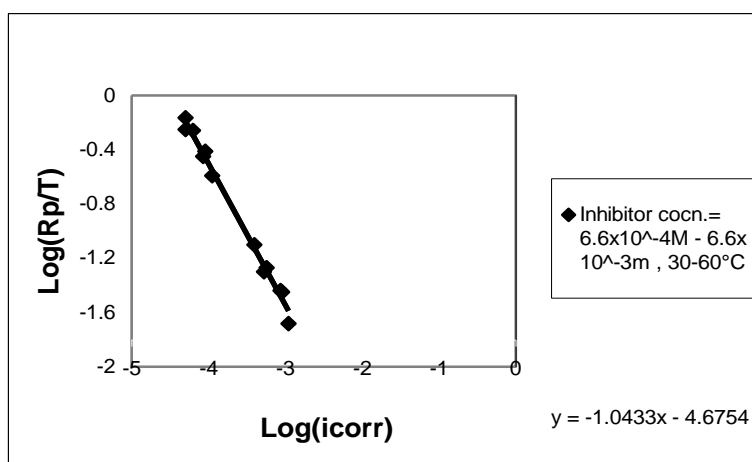


Fig.5 Plot of polarization resistance data in 3N HCl acid solution.

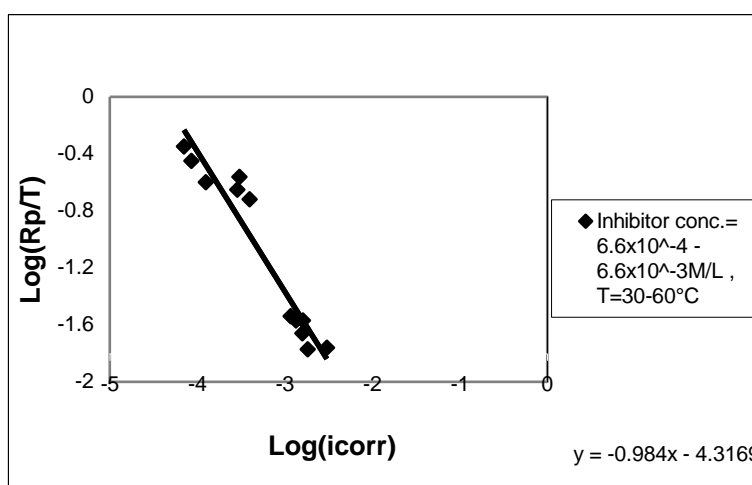


Fig.6 Plot of polarization resistance data in 5N HCl acid solution.

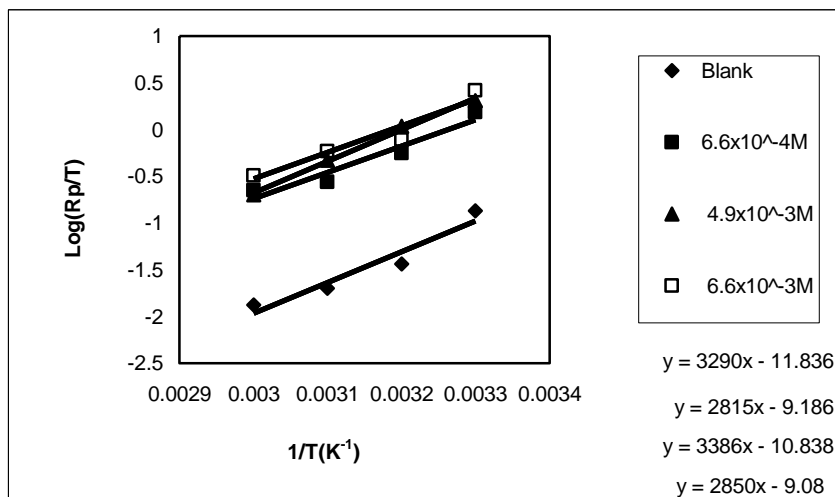


Fig 7 Plots of Log(Rp/T) V's 1/T in absence and presence of various conc. of inhibitor in 1N HCl acid.

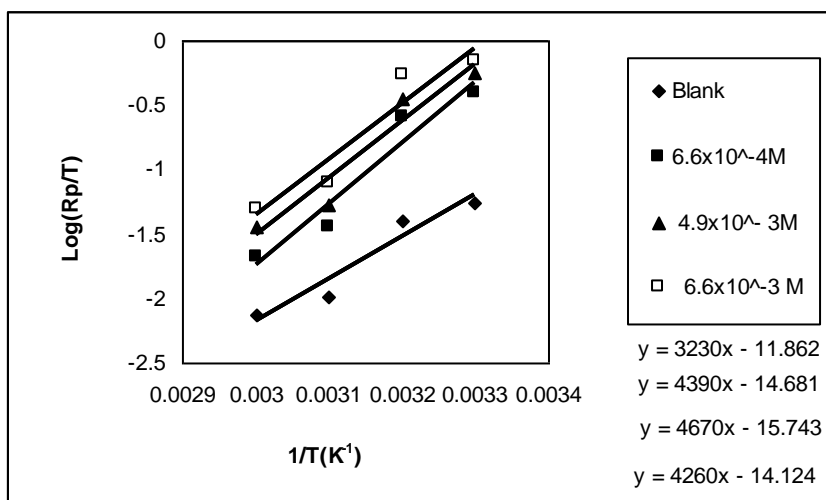


Fig 8 Plots of Log(Rp/T) V's 1/T in absence and presence of various conc. of inhibitor in 3N HCl acid.

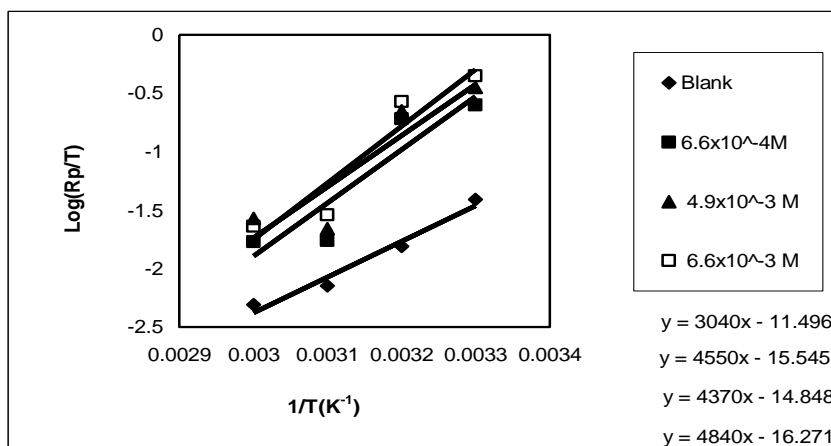


Fig 9 Plots of Log(Rp/T) V's 1/T in absence and presence of various conc. Of inhibitor in 5N HCl acid.





## CONCLUSIONS

- PHTU acted as efficient corrosion inhibitor for carbon steel in 1,3, and 5 N HCl acid concentrations.
- The results obtained by Betacrunch technique are thought to be in good agreement with those if obtained experimentally since corrosion potential is far from the equilibrium potentials of both H<sub>2</sub> evolution and metal dissolution reactions.
- For a certain temperature the polarization resistance decreases with acid concentration increase, while increases with inhibitor concentration increase.
- For a certain acid concentration, the polarization resistance decreases with temperature increase in absence and presence of inhibitor.
- The inspection of data in Table(6) reveal that the activation energy of the corrosion reaction in absence of inhibitor(PHTU) is approximately the same and is acid concentration independent.
- The average activation energy value of (57.8 kJ/mole) for 1 N- HCl inhibitor system support the fact that the inhibitor is physically adsorbed on the metal surface, although the increase in inhibition efficiency is not so pronounced.
- The experimental result indicates generally that the energy barrier of corrosion reaction in 3 , and 5 N- HCL inhibitor system increase as the concentration of PHTU is increased, since the value of activation energy increase with an increase in PHTU. This suggests that the process is activation controlled and the mechanism of the inhibitor adsorption in this case is chemical adsorption. i.e; 85 and 87.8 kJ/mole is > than 80 kJ /mole

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