Int. J. Electrochem. Sci., 5 **(2010)** 1516 - 1526

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

The Effect of Temperature on the Corrosion of Cu/HNO_3 in the Presence of Organic Inhibitor: Part-2

A. Zarrouk[1], *I. Warad*[2], *B. Hammouti*[1,*], *A Dafali*[1], *S.S. Al-Deyab*[2], *N. Benchat*[1]

[1] LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, B.P. 717, 60000 Oujda, Morocco.
[2] Department of Chemistry - College of Science, King Saud University, B.O. 2455 Riaydh 11451 Saudi Arabia
[*]E-mail: hammoutib@gmail.com

Received: 11 August 2010 / *Accepted:* 19 August 2010 / *Published:* 1 October 2010

The effect of temperature on the corrosion behaviour of copper in 2M nitric acid solution in the presence and absence of 5-(2,6-dichlorobenzyl)-6-methylpyridazin-3(2*H*)-one (P3) has been investigated by weight loss method. The inhibitory effect increases with increasing inhibitors concentration and decreases with rise of temperature from 303 to 343K. Adsorption follows the Langmuir isotherm with negative values of free enthalpy suggesting a spontaneous adsorption process. Other thermodynamic parameters such as, equilibrium constant, adsorption heat and adsorption entropy were obtained. The various parameters of activation determining the kinetic data such as energy, enthalpy and entropy at different concentrations of the inhibitor were evaluated and discussed.

Keywords: Corrosion, inhibition, pyridazine, activation, adsorption.

1. INTRODUCTION

Pure copper is a very soft, malleable metal. It is alloyed with small quantities of metals such as Be, Te, Ag, Cd, As, and Cr to modify the properties for particular applications, while retaining many of the characteristics of the pure metal. The reasons for this enormous consumption of copper plumbing tube are its excellent corrosion resistance, its ease of fabrication during installation, and hence low-installation costs, and additionally, its contribution to health and the maintenance of healthy water. Further, copper is seen as environmentally friendly due to its potential to be 100% recycled [1]. Copper suffer from general corrosion in nitric acid, the corrosion rate is quite high both in weak and high nitric acid because of higher solubility of copper nitrate. The addition of efficient organic inhibitors is quite necessary to ovoid much attack of copper in nitric acid.

Among the different factors affecting the corrosion rate, the temperature may clearly be important in determining the form, extent and rate of the reaction. The effect of temperature on the corrosion inhibition of various organic compounds was treated by several works [2-4]. Investigations attempt to describe the corrosion phenomena of metals in aggressive media in the presence and absence of inhibitor. Also, the possible structural modifications of the double layer and the partial action of inhibitor on the electrochemical reactions are discussed [4-6]. The most effective and efficient inhibitors are organic compounds having heteroatoms and/or π bonds in their structures. An efficient organic compound possesses the ability to be adsorbed on the metal surface by displacing water molecule from a corroding interface as follow:

$$\mathrm{Org}_{(sol)} + \mathrm{nH_2O}_{(ads)} \rightarrow \mathrm{Org}_{(ads)} + \mathrm{nH_2O}_{(sol)}$$

The adsorption of inhibitor is influenced by the electronic structure of the inhibiting molecules [7-9] and also by the steric factors, aromaticity, electron density at the donor atoms and also by the presence of functional groups such as C=NH, –N=N–, –CHO, R–OH, C=C, etc.

N-heterocyclic compounds receive more and more attention in inhibitory practices to avoid corrosion damage of metals and alloys [10–12]. Adsorption of inhibitors creates a barrier against aggressive ions to reach metallic surface and hence reduce the corrosion rate. Inhibitor molecules then impede by blocking the reactive sites on the surface.

Survey of literature shows that pyridazine compounds are efficient inhibitors on the corrosion of metals in acid solution [10-14]. This paper is aimed to study the influence of temperature on the corrosion of copper in HNO_3 solution at different concentration of 5-(2, 6-dichlorobenzyl)-6-methylpyridazin-3(2*H*)-one (P3). The molecular structure of P3 is shown in Fig. 1. The thermodynamic parameters describing the kinetic of corrosion as well as adsorption process when varying temperature and inhibitor concentration are evaluated and discussed.

2. EXPERIMENTAL DETAILS

Copper strips containing 99.5 wt.% Cu, 0.001wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities was used. Prior to all measurements, are abraded with a series of emery paper from 180 to 2000 grade.

The specimens are washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (2M HNO_3) was prepared by dilution of Analytical Grade 67 % HNO_3 with double-distilled water. Pyridazine compound was synthesised, purified and characterised as described previously [15].

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 50 cm^3. The copper specimens used have a rectangular form (2cm × 2cm × 0.20cm). The immersion time for the weight loss is 1h.

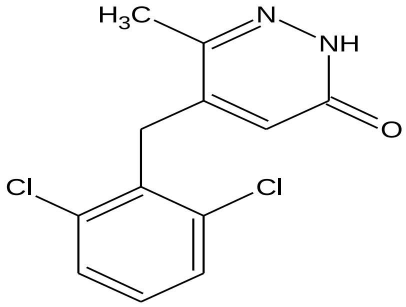

Figure 1. The molecular structure of the tested pyridazine derivative (P3)

3. RESULTS AND DISCUSSION

3.1. Effect of temperature

Table 1 gathers the values of corrosion rate of Cu/2M HNO_3 at different concentrations of P3 were determined by weight loss measurement at various temperatures (303-343 K) and the corresponding inhibition efficiencies.

It is well-known that corrosion rate increases with the rise of temperature in acidic media. At each temperature, the inhibition corrosion increases with inhibitor concentration. But at a given inhibitor concentration, the inhibitory effect ceases more and more to jump from 96.2% at 303 K to 54.7% at 343 K. Apparently, the results obtained postulate that the inhibitor function through adsorption on the copper surface by the blocking the active sites to form a screen onto the copper surface from acidic solution. As the temperature increases, we notice the desorption rate manifests parallel to that of adsorption; the surface becomes less protected and then the inhibitor gradually loss its effectiveness.

3.2. Kinetic parameters of activation

The influence of temperature on the kinetic process of corrosion in free acid and in the presence of adsorbed inhibitor leads to get more information on the electrochemical behaviour of metallic materials in aggressive media. The corrosion reaction of copper in nitric acidic media depends on temperature. The dependence of the rate constant k of chemical reactions on the temperature T is expressed by the Arrhenius law:

$$k = Ae^{-E_a/RT} \tag{1}$$

where *A* is the pre-exponential factor or simply the prefactor and R is the gas constant. The units of the pre-exponential factor are identical to those of the rate constant.

Equation (1) was first proposed by Van’t Hoff in 1884; five years later in 1889, Arrhenius provided a physical justification and interpretation for it. Nowadays it is best seen as an empirical relationship. The Arrenhius law may be presented as a straight line of the logarithm of the corrosion rate (W) and 1/T as pointed out by Putilova [16] according to the following relation:

$$\ln W = \frac{-E_a}{RT} + \ln A \qquad (2)$$

Table 1. Gravimetric data of P3 at different concentration in 2M HNO_3 at different temperatures.

T (K)	Concentration(M)	W(mg/cm^2.h)	Ew (%)
303	10^{-3}	0.068	**96.2**
	5×10^{-4}	0.131	92.6
	10^{-4}	0.176	90.1
	5×10^{-5}	0.617	65.3
313	10^{-3}	0.366	**95.0**
	5×10^{-4}	0.741	89.9
	10^{-4}	1.675	77.2
	5×10^{-5}	3.271	55.4
323	10^{-3}	3.686	**85.2**
	5×10^{-4}	5.240	79.0
	10^{-4}	7.591	69.6
	5×10^{-5}	15.082	39.6
333	10^{-3}	20.503	**71.1**
	5×10^{-4}	29.319	58.6
	10^{-4}	36.184	48.9
	5x10^{-5}	50.105	29.3
343	10^{-3}	84.524	**54.7**
	5×10^{-4}	10.437	43.5
	10^{-4}	123.15	34.0
	5×10^{-5}	146.38	21.6

The linear regression plots between ln (W) and 1/T are presented in Fig.2. The calculated activation energies, E_a, and pre-exponential factors, A, at different concentrations of the inhibitor are collected in Table 2. The change of the values of the apparent activation energies may be explained by the modification of the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [17].

Literature [17-19] discussed the variation of the apparent activation energy E_a in the presence and absence of inhibitor. Higher values for E_a were found in the presence of inhibitors. Other studies [16, 20, 21] showed that in the presence of inhibitor the apparent activation energy was lower than that in the absence of inhibitor. However, in our study, E_a increases with increasing the P3 concentration, and all values of E_a were higher than that in the absence of pyridazine compound. This type of inhibitor retards corrosion at ordinary temperatures but inhibition is diminished at elevated temperature.

Arrhenius law predicts that corrosion rate increases with the temperature and E_a and A may vary with temperature (Eq. 1). The obtained values seem that A and Ea increase continuously with the inhibitor's concentration.

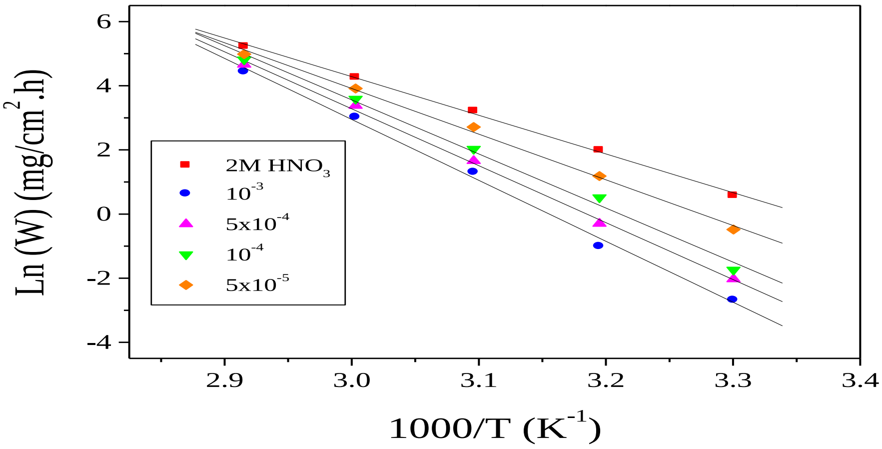

Figure 2. Arrhenius plots of copper in acid with and without different concentrations of P3

Table 2. Some activation parameters of Cu/HNO_3 at different concentrations P3.

Concentration of P3 (M)	*Pre-exponential factor (mg/cm^{2}h)*	*Linear regression coefficient (r)*	*E_a (kJ/mol)*	*ΔH_a° (kJ/mol)*	*ΔS°_a (J/mol.K)*	*E_a - ΔH_a° (kJ/mol)*
Blank	3.6627×10^{17}	0.99908	100.21	97.53	82.36	**2.68**
5×10^{-5}	1.8026×10^{20}	0.99832	118.41	115.73	133.90	**2.68**
10^{-4}	3.3215×10^{23}	0.99703	140.23	137.55	196.41	**2.68**
5×10^{-4}	3.5186×10^{24}	0.99898	147.54	144.86	216.03	**2.68**
10^{-3}	**1.0924×10^{26}**	**0.99805**	**157.98**	**155.30**	**244.59**	**2.68**

Other kinetic data (enthalpy and entropy of corrosion process) are accessible using the alternative formulation of Arrhenius equation [14]:

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S_{\mathrm{a}}^{o}}{R}\right)\exp\left(-\frac{\Delta H_{\mathrm{a}}^{o}}{RT}\right) \qquad (3)$$

where h is plank's constant, N is Avogrado's number, ΔS_a° and ΔH_a° are the entropy and enthalpy of activation, respectivel. Plots of ln (W/T) vs. the reciprocal of temperature show straight lines with a slope equal to ($-\Delta H_a^{\circ}/R$) and an intercept of (Ln R/Nh + $\Delta S_a^{\circ}/R$). The values of ΔH_a° and ΔS_a° are also presented in Table 2.

Inspection of the kinetic data obtained in Table 2 shows that all parameters of corrosion process increases with the inhibitor concentration. Literature postulates that the positive sign of the enthalpy (ΔH_a°) is an endothermic nature of the copper dissolution process. The entropy of activation ΔS_a^{0} in the absence of inhibitors is positive and this value increases positively with the P3 concentration. The increase of ΔS_a° implies that an increase in disordering takes place on going from reactants to the activated complex [19].

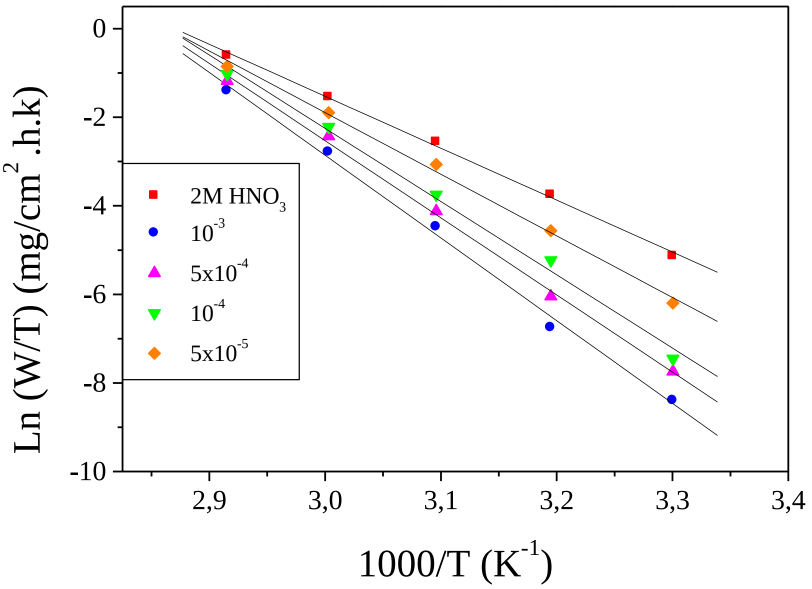

Figure 3. The relationship between Ln (W/T) and T^{-1} for different concentrations of P3.

The increase of E_a and $\Delta H°_a$ with an increase in the P3 concentration (Fig. 4) suggests that the energy barrier of corrosion reaction increases with the inhibitor's concentration. The higher activation energy in the inhibitor's presence further supports the proposed physisorption mechanism.

Unchanged or lower values of Ea in inhibited systems compared to the blank to be indicative of chemisorption mechanism, while higher values of E_a suggest a physical adsorption mechanism. This type of inhibitors retards the corrosion process [22,23].

It is also interested to verify the known thermodynamic relation between E_a and ΔH_a^0 [21]:

$$E_a - \Delta H_a^{\circ} = RT \tag{4}$$

The calculate values are too close to RT is 2.68 kJ/mol at 323 K. This result shows the inhibitor acted equally on E_a and ΔH_a°.

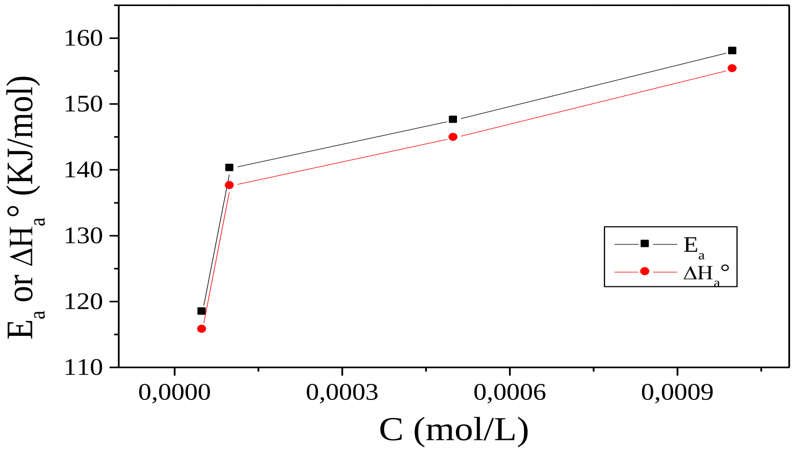

Figure 4. The relationship between E_a and ΔH_a° with concentration of P3.

3.3. Thermodynamic parameters and adsorption isotherm

Attempts were made to fit values of Θ to many isotherm including Langmuir, Temkin, Frumkin and Freundlich. The well known is that of Langmuir (1916), who put forward the first quantitative theory of the adsorption of a gas, assumed that a gas molecule condensing from the gas phase would adhere to the surface for a short time before evaporating and that the condensed layer was only one atom or molecule thick.

If Θ is the fraction of the surface area covered by adsorbed molecules at any time, the rate of desorption is proportional to Θ and equal to $k_d\Theta$ where k_d is a constant at constant temperature. Similarly the rate of adsorption will be proportional to the area of bare surface and to the rate at which the molecules strike the surface (proportional to the gas pressure p). At equilibrium the rate of desorption equals the rate of adsorption:

$$k_d \Theta = k_a (I - \Theta) p \tag{5}$$

and the Langmuir isotherm can be expressed as:

$$\frac{\Theta}{1-\Theta} = \left(\frac{k_a}{k_d}\right) p = ap \tag{6}$$

where a is a constant, the Langmuir constant or adsorption coefficient [24].

At any metal/solution interfaces, the Langmuir adsorption isotherm written in the rearranged form:

$$\frac{C}{\Theta} = \frac{1}{K} + C \text{ with } K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{7}$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, Θ is the surface coverage and the standard adsorption free energy (ΔG_{ads}).

The relationship between C/Θ and C presents linear behaviour at all temperatures studied (Fig. 5) with slopes equal to unity.

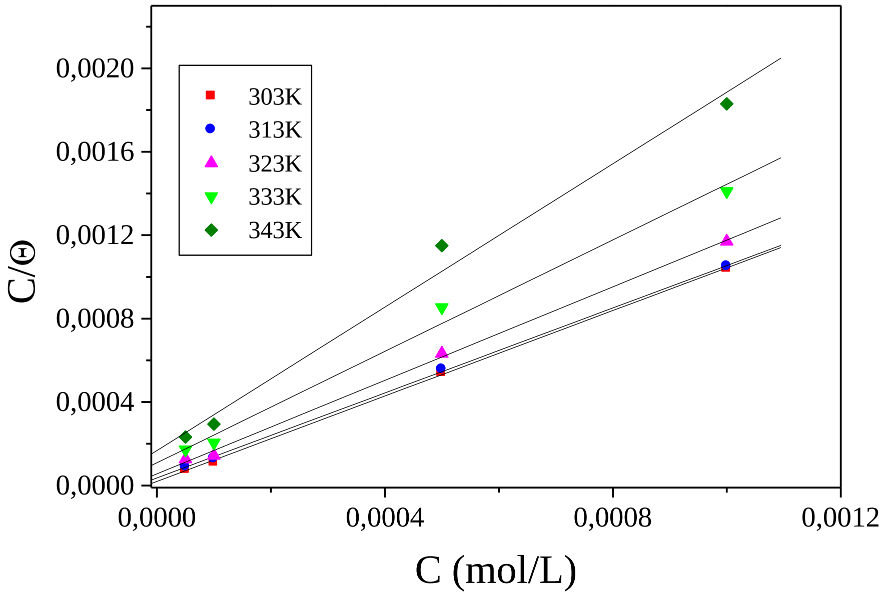

Figure 5. The relationship between C/Θ and C of P3 at various temperatures

To get more adsorption enthalpy, ΔH°_{ads}, the Van't Hoff equation was used [25]:

$$\ln(K) = -\frac{\Delta H^{\circ}_{ads}}{RT} + Constant \tag{8}$$

The straight line obtained between ln (K) and 1/T leads to $\Delta H^{\circ}_{ads} = -46.8$ kJ.mol^{-1} which is equal to that estimated by the Gibbs–Helmholtz equation, expressed by:

$$\left[\frac{\partial(\Delta G^{\circ}_{ads}/T)}{\partial T}\right]_P = -\frac{\Delta H^{\circ}_{ads}}{T^2} \tag{9}$$

and written in the following equation.

$$\frac{\Delta G^{\circ}_{ads}}{T} = \frac{\Delta H^{\circ}_{ads}}{T} + A \qquad (10)$$

The standard adsorption entropy ΔS°_{ads} may be deduced using the thermodynamic basic equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \qquad (11)$$

All the obtained thermodynamic parameters are shown in Table 3. The negative values of ΔG°_{ads} for P3 indicate the spontaneous of the adsorption of P3 and stability of the adsorbed layer on the copper surface. More negative value designates that inhibitor is strongly adsorbed on the copper surface. The negative values of ΔH°_{ads} also show that the adsorption of inhibitor is an exothermic process [26]. It assumed that an exothermic process is attributed to either physical or chemical adsorption but endothermic process corresponds solely to chemisorption. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of a physisorption process is lower than 40 kJ mol^{-1} while the adsorption heat of a chemisorption process approaches 100 kJ mol^{-1} [27]. In this study; the standard adsorption heat -46.80 kJmol^{-1} postulates that a physical adsorption is more favoured. The negative values of ΔS^{o}_{ads} is generally explained an ordered of adsorbed molecules of inhibitor with the progress in the adsorption onto the copper surface [28].

Literature pointed that values of ΔG°_{ads} around -20 kJ.mol^{-1} or lower are related to the electrostatic interaction between the charged molecules and the charged metal (physisorption); those around -40 kJ.mol^{-1} or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [29,30]. The obtained values of ΔG°_{ads} surrounded -40 kJ.mol^{-1} indicating, that the adsorption mechanism of the pyridazine tested on copper in 2M HNO_3 solution was typical of physical adsorption (Table 3).

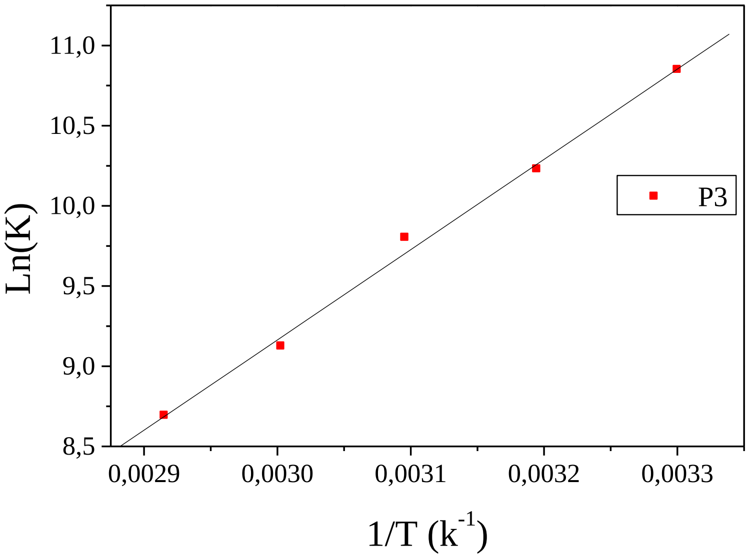

Figure 6. The relationship between ln(K) and 1/T for P3

The variation of $\Delta G^\circ_{ads}/T$ with 1/T gives a straight line with a slope that equals ΔH°_{ads} = -46.80 (kJ/mol) (Fig. 7). It can be seen from the figure that $\Delta G^\circ_{ads}/T$ decreases with 1/T in a linear fashion.

Table 3. Thermodynamic parameters of adsorption of P3 on the steel surface at different temperatures.

	Linear regression coefficient (r)	K	ΔG°_{ads} (kJ/mol)	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol.K)
303	0.99981	51396.44	-37.44	-46.80	-30.89
313	0.99984	27644.70	-37.07		-31.09
323	0.99927	18050.80	-37.10		-30.03
333	0.99582	9163.22	-36.38		-31.29
343	0.99395	5950.7	-36.24		-30.79

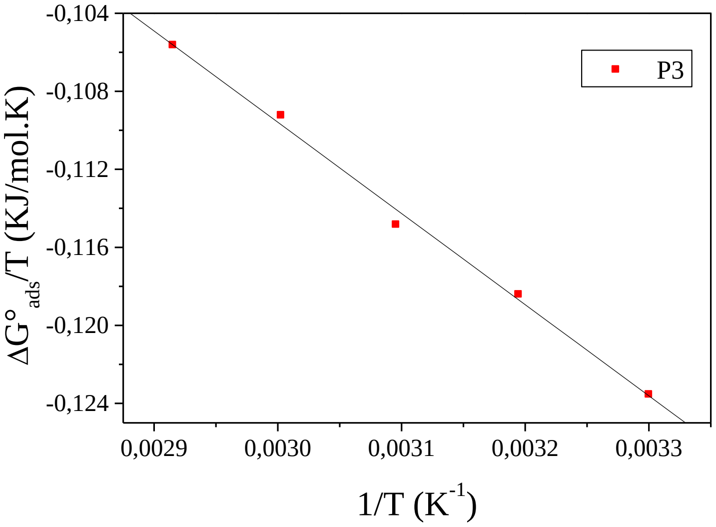

Figure 7. Relationship between $\Delta G^\circ_{ads}/T$ and the reverse of absolute temperature

4. CONCLUSION

* Results obtained show that pyridazine tested is an efficient inhibitor.
* Inhibition efficiency increases with the increase of concentration to attain 96.2% at 10^{-3}M.
* Increase of temperature leads in a decrease of efficiency and an increase of the activation corrosion energy.
* P3 adsorbs according to the Langmuir isotherm model and the negative value of ΔG°_{ads} is a sign of spontaneous adsorption on the metal surface.
* Kinetic and adsorption parameters were evaluated and discussed.

References

1. Uhlig's Corrosion Handbook, Second Edition, Edited by R. Winston Revie, ISBN 0-471-15777-5, (2000), John Wiley & Sons, Inc. p.729
2. E.A. Noor, A.H. Al-Moubaraki, *Mater. Chem. Phys.*, 110 (2008) 145.
3. M. Spah, D. C. Spah, B. Deshwal, S. Lee, Y-K. Chae, J. W. Park , *Corros. Sci.*, 51 (2009)1293.
4. M. Abdallah, M. Al- Agez, A.S. Fouda, *Int. J. Electrochem. Sci.*, 4 (2009) 336.
5. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.*, 45 (2003) 33.
6. M. Benabdellah, K.Tebbji, B. Hammouti, R. Touzani, A. Aouniti, A. Dafali, S. Elkadiri, *Phys. Chem. News.*, 43 (2008) 115.
7. S. S. Abd El Rehim, M. A. M. Ibrahim, K. F. Khalid, *J. Appl. Electrochem.*, 29 (1999) 593.
8. I. Zaafarany, M. Abdallah, *Int. J. Electrochem. Sci.*, 5 (2010) 18.
9. Nageh Allam, *Appl. Surf. Sci.*, 253 (2007) 4570.
10. M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti, S. Kertit, *Materials Letters.*, 60 (2006) 1901.
11. A. Chetouani, B. Hammouti, A. Aouniti, N. Benchat, T. Benhadda, *Prog. Org. Coat.*, 45 (2002) 373.
12. Deana Wahyuningrum, Sadijah Achmad, Yana Maolana Syah, Buchari, Bunbun Bundjali, Bambang Ariwahjoedi, *Int. J. Electrochem. Sci.*, 3 (2008) 154..
13. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagrenée, H. Vezin, F. Bentiss, *Org. Coat.*, 51 (2004) 118.
14. A. Zarrouk, A. Chelfi, A. Dafali, B. Hammouti, S. S. Al-Deyab, I. Warad, N. Benchat, M. Zertoubi, *Int. J. Electrochem. Sci.*, 5 (2010) 696.
15. A. O. Kappe, D. Dallinger, *Nat. Rev. Drug. Discov.*, 5 (2006) 51
16. N. Putilova, S. A. Balezin, V. P. Barannik, *Metallic Corrosion Inhibitors, Pergamon Press, Oxford*, (1960)
17. O. Riggs, I. R. Hurd, M. Ray, *Corrosion.*, 23 (1967) 252.
18. T. P. Zhao, G. N. Mu, *Corros. Sci.*, 41 (1999)1937.
19. A. Abd-El-Nabey, E. Khamis, M. Sh. Ramadan, A. El-Gindy, *Corrosion.*, 52 (1996) 671.
20. S. N. Banerjee, S. Misra, *Corrosion.*, 45 (1989) 780.
21. Q. H. Cai, Y. K. Shan, B. Lu, X. H. Yuan, *Corrosion.*, 49 (1993) 486.
22. Elouali, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E. M. Essassi, M. Bouachrine, *J. Mater. Environ. Sci.*, 1 (2010) 1.
23. M. Bouklah, B. Hammouti, M. Lagrenée, F. Bentiss, *Corros. Sci.*, 48 (2006)2831.
24. L.L. Shreir, R.A. Jarman, G.T. Burstein, Corrosion, Metal/Environment Reactions, Vol.2 Butterworth Heinemann, ISBN 0 7506 1077 8, (2000) p. 20 :33.
25. Tebbji, N. Faska, A. Tounsi, H. Oudda, M. Benkaddour, B. Hammouti, *Mater. Chem. Phys.*, 106 (2007) 260.
26. C. Emregul, M. Hayvali, *Corros. Sci.*, 48 (2006) 797.
27. A. Zarrouk, A. Dafali, B. Hammouti, H. Zarrok, S. Boukhris, M. Zertoubi, *Int. J. Electrochem. Soc.*, 5 (2010) 46.
28. R. Arshadi, M. Lashgari, Gh. A. Parsafar, *Mater. Chem. Phys.*, 86 (2004) 311.
29. Ousslim, A. Aouniti, K. Bekkouch, A. Elidrissi, B. Hammouti, *Surf. Rev. Let.*, 16 (2009) 609
30. Dahmani1, A. Et-Touhami, S.S. Al-Deyab, B. Hammouti, A. Bouyanzer, *Int. J. Electrochem. Sci.*, 5 (2010) 1060.