



Scholars Research Library

Der Pharma Chemica, 2012, 4(5):1887-1896

(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Adsorption and corrosion inhibition of some tripodal compounds for mild steel in molar hydrochloric acid medium

B. Zerga¹, M. Sfaira^{1*}, M. Taleb¹, M. Ebn Touhami², B. Hammouti³, A. Attayibat⁴, S. Radi⁴, A. T. Benjelloun¹

¹ Laboratoire d'Ingénierie des Matériaux, de Modélisation et d'Environnement, LIMME, Faculté des Sciences Dhar El Mahraz, Université Sidi Mohammed Ben Abdellah, USMBA, BP 1796 – 30000, Atlas – Fès, Morocco.

² Laboratoire des Matériaux, Electrochimie et Environnement, Faculté des Sciences, Université Ibn Tofaïl, BP. 133 – 14000, Kénitra, Morocco.

³ LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, BP 717 – 60000, Oujda, Morocco.

⁴ Laboratoire de Chimie Organique, Macromoléculaire et Produits Naturels, Faculté des Sciences, BP 524, Oujda – Morocco.

ABSTRACT

The inhibition effects of 2-[N,N-bis[(5-methyl-1-pyridin-2-yl)-1H-pyrazol-3-yl)methyl] amino} ethanol (PPN) and 3-[N,N-bis(thien-2-ylmethyl)amino]propan-1-ol (TTN) on the corrosion of mild steel in 1 M hydrochloric acid solution were investigated by weight loss and electrochemical polarization curves. The results revealed that both products were very good inhibitors at very low concentration and acted as mixed-type inhibitors. The adsorption of PPN and TTN on mild steel surface basically obeyed to the Langmuir adsorption isotherm model. The effect of temperature on the corrosion behaviour of mild steel was also studied in the temperature range 25-80°C. The thermodynamic parameters such as adsorption heat ($\Delta_{ads}H^0$) and adsorption free energy ($\Delta_{ads}G^0$) were calculated and discussed.

Keywords: Corrosion inhibition, tripod, Polarisation curves, Weight loss, Mild steel.

INTRODUCTION

Hydrochloric acid is widely used for the removal of rust and scale in several industrial processes. The corrosion of steel and ferrous alloys in such environments and its inhibition constitute a complex problem. Various types of organic compounds are widely used as corrosion inhibitors for materials protection against deterioration from corrosion. A perusal of the literature on acid corrosion inhibition reveals that most organic substances employed as corrosion inhibitors act by adsorption on the metal surface. The adsorption mainly depends on the presence of π -electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of mild steel [1-11]. The influence of the inhibitor upon metal corrosion is often associated with physical or chemical adsorption.

The compounds containing both nitrogen and sulphur can provide excellent inhibition compared with compounds containing only nitrogen or sulphur [6]. In recent years, N- and S-containing triazole derivatives have attracted more attention for their excellent corrosion inhibition performance [12-14]. Not only can some N- and S-containing triazole compounds give very high values of inhibition efficiency, but they can bring down the hydrogen permeation current to a considerable extent [12]. Hackerman [14] gave the idea that higher percentage of π -orbital of the free electrons on the N-atom leads to inhibitive action. The N-containing compounds used as acid inhibitors include heterocyclic bases such as pyridine, quinoline, and various amines [15]. The influence of some heterocyclic compounds containing more than one nitrogen atoms in their molecules, on corrosion of mild steel in acid solutions, was investigated [6-11] with a view to establish correlation among the examined substances between molecular structure and inhibition efficiency of various compounds.

The aim of this paper was to study the inhibiting action of newly tripod compounds, namely 2- $\{N,N$ -bis[(5-methyl-1-pyridin-2-yl-1*H*-pyrazol-3-yl)methyl]amino} ethanol and 3- $\{N,N$ -bis(thien-2-ylmethyl)amino}propan-1-ol and denoted hereafter PPN and TTN, respectively. The anticorrosion behaviour of mild steel in 1 M HCl medium in the absence and presence of the tripod inhibitors has been studied by gravimetric method and potentiodynamic polarisation curves. The thermodynamic parameters of the undertaken inhibitors adsorption onto the mild steel were determined and the nature of inhibitors adsorption process was also studied and discussed.

MATERIALS AND METHODS

2.1. Material preparation

Mild steel strips composed of: 0.09 wt.% P, 0.38 wt.% Si, 0.01 wt.% Al, 0.05 wt.% Mn, 0.21 wt.% C, 0.05 wt.% S and balance iron were pre-treated prior to all experiments by grinding with emery paper SiC (grades 400 to 1200), then cleaned with ethanol, rinsed with distilled water and finally dried at room temperature before use. The solutions (1 M HCl) were prepared by dilution with distilled water. The tested inhibitors, namely 2- $\{N,N$ -bis[(5-methyl-1-pyridin-2-yl-1*H*-pyrazol-3-yl)methyl]amino}ethanol (PPN) and 3- $\{N,N$ -bis(thien-2-ylmethyl)amino}propan-1-ol (TTN) were synthesised according to a previously described experimental procedure [16,17]. The molecular structures of these products are shown in Fig. 1. The concentration range of these inhibitors employed was 10^{-6} to 10^{-3} M.

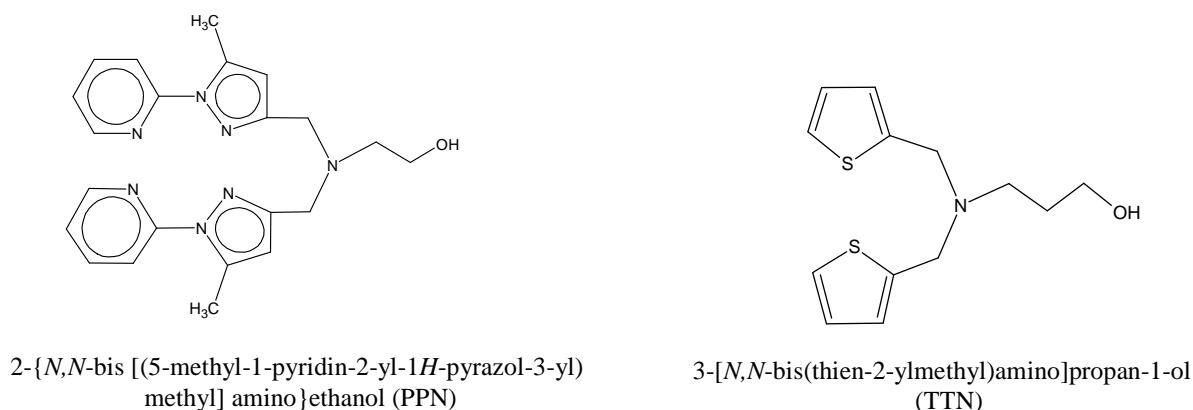


Fig. 1. Chemical formula of both inhibitors

2.2. Weight loss method

2.2. Weight loss measurements

Gravimetric experiments were carried out in a double glass cell equipped with a thermostatic cooling condenser. The solution volume was 100 mL. The steel specimens used have a rectangular form (length =2 cm, width =1cm, thickness =0.2cm). The duration of tests was 6 h at 25°C in aerated solutions. At the end of the tests, the specimens were carefully washed and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss was reported. Weight loss allowed calculation of the mean corrosion rate in $\text{mg cm}^{-2} \text{h}^{-1}$.

The inhibition efficiency (IE%) of PPN and TTN on the corrosion of mild steel was calculated as follows:

$$IE_{WL} \% = \frac{W_0 - W}{W_0} \times 100 \quad (1)$$

W_0 and W are the values of the average weight loss without and with addition of the inhibitors, respectively.

2.3. Current-voltage I-E measurements

Electrochemical experiments were carried out using Volta Lab PGZ100 and controlled with corrosion analysis software (Voltmaster 4). Polarisation measurements were obtained using a conventional three-electrode cell with a capacity of 500 mL. The working electrode (WE), in the form of a disc cut from steel, had a geometrical area of 1 cm² and was embedded in polytetrafluoroethylene (PTFE) to avoid any infiltration of electrolyte. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrode, respectively. All tests were performed in aerated solutions under continuously stirred conditions at 25 °C.

The anodic and cathodic polarisation curves were recorded by a constant sweep rate of 1 mV s⁻¹. The data in the Tafel region (-750 to -250 mV versus corrosion potential), except in the vicinity of corrosion potential, E_{corr} , have been processed for evaluation corrosion kinetic parameters evaluation by plotting $\log I$ versus E curves.

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$IE_{I-E} \% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \quad (2)$$

Where $I_{corr(inh)}$ and I_{corr} are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of Tafel lines to the corresponding corrosion potential.

RESULTS AND DISCUSSION

3.1. Adsorption and corrosion inhibition of PPN and TTN

Table 1 gives the values of the inhibition efficiency obtained from weight loss measurements of mild steel at different concentrations of TTN and PPN in 1 M HCl at 25 °C after 6 hours of hold time immersion. Two tests of corrosion weight loss are realized and apparent precision resulting from used material and reproducibility is esteemed to 8%.

The inhibition efficiency increases with the increase of inhibitors concentration. The maximum $IE_{WL}\%$ is approximately 97% with TTN at 25 °C. This behaviour can be attributed to the increase of the surface area covered by the adsorbed molecules of inhibitors with the increase of their concentration. It is generally assumed that the adsorption of the inhibitors at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media.

Table 1: Corrosion weight loss of mild steel in the blank solution and added of PPN and TTN at different concentrations after 6 h of immersion at 25 °C.

Inhibitor	Concentration mol L ⁻¹	W_{corr} mg cm ² h ⁻¹	IE_{WL} %
HCl	0	1,76	—
PPN	10 ⁻⁶	0.75	57.4
	10 ⁻⁵	0.48	72.4
	5×10 ⁻⁵	0.34	80.5
	10 ⁻⁴	0.20	88.6
	5×10 ⁻⁴	0.11	93.8
	10 ⁻³	0.09	94.9
TTN	10 ⁻⁶	0.65	63.1
	10 ⁻⁵	0.43	75.6
	5×10 ⁻⁵	0.26	85.3
	10 ⁻⁴	0.15	91.5
	5×10 ⁻⁴	0.09	94.9
	10 ⁻³	0.06	96.6

Four types of adsorption may take place by organic molecules at the metal/solution interface: (1) electrostatic attraction between the charged metal and the charged molecules, (2) interaction of uncharged electrons pair in the molecule with the metal, (3) interaction of π electrons with the metal and (4) combination of (1 and 3) [18]. Chemisorption involves the share or transfer of charge from the molecules to the surface to form a coordinate type bond. Electron transfer is typical for transition metals having vacant low energy electron orbital. As for inhibitors, the electron transfer can be expected with compounds having relatively loosely bound electrons [19].

Fig. 2 shows the variation of $IE_{WL}\%$ with concentration of PPN and TTN for mild steel in 1 M HCl in the range of temperature from 40 °C to 80 °C. Both PPN and TTN inhibited the corrosion of steel with relatively small concentration. Figure 2 also exemplifies that the inhibition efficiency increases with the inhibitors concentration in the range of the studied temperatures. When the concentration reaches approximately 10^{-4} M, the $IE_{WL}\%$ reaches certain values and do not change obviously for PPN inhibitor whereas it decreases continually even at higher concentrations for TTN with rise of temperature.

Two modes of adsorption can be considered. The process of physical adsorption requires the presence of electrically charged metal surface and the charged species in the bulk of the solution. Chemisorption process involves charge sharing of charge transfer from the inhibitor molecules to the metal surface. This is possible in case of positive as well as negative charges on the surface. The presence of a transition metal, having vacant, low-energy electron orbital, and an inhibitor molecule having relatively loosed bound electrons or heteroatoms with lone-pair electrons facilitates this adsorption [7]. On the other hand, PPN and TTN which possess nitrogen, sulphur and oxygen atoms and lone-pair electrons can accept a proton, leading to the cationic forms. These species can adsorb on the metal surface because of attractive forces between the negatively charged metal and the positively inhibitors. In our case, PPN as it temperature-independent may be adsorbed predominantly by chemisorption whereas for TTN which its inhibiting efficiency decreases dramatically with temperature may essentially act by physisorption.

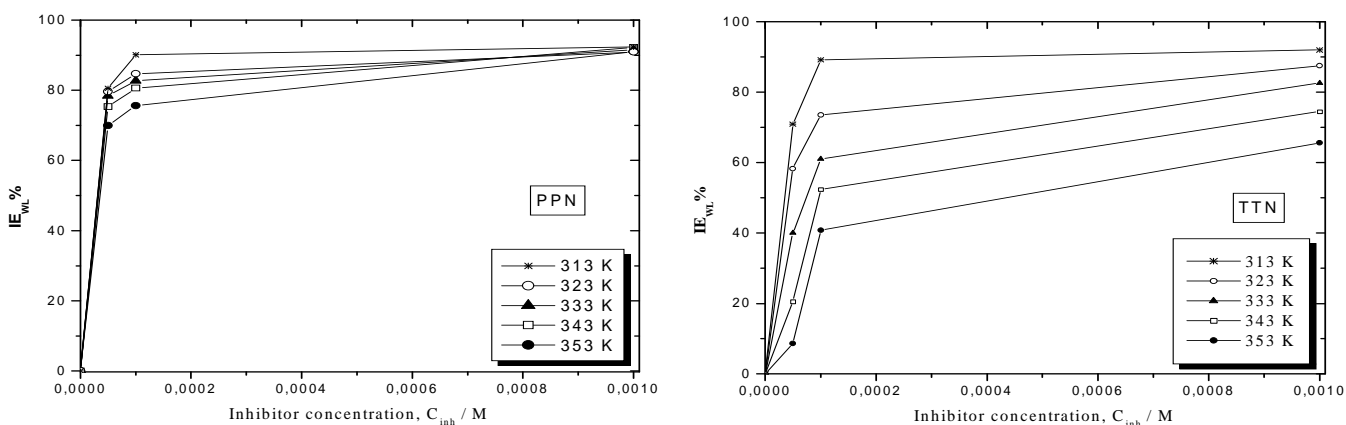


Fig. 2: Variation of $IE_{WL}\%$ with concentration of PPN and TTN for mild steel at different temperatures.

A correlation between the surface coverage θ and the inhibitors concentration C_{inh} in the electrolyte can be represented by the Langmuir adsorption isotherm model [20]:

$$\theta = \frac{K_{ads} C_{inh}}{1 + K_{ads} C_{inh}} \quad \text{or} \quad \frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (3)$$

Where C_{inh} is the concentration of inhibitor, K_{ads} is the adsorptive equilibrium constant. θ is calculated from the following relation [21,22]:

$$\theta = \frac{W_0 - W}{W_0 - W_m} \quad (4)$$

W and W_0 are the weight loss, in hydrochloric acid solution, with and without addition of inhibitors, respectively and W_m is the smallest weight loss.

The plots of C_{inh}/θ versus inhibitors concentration C_{inh} , at different temperatures, show a linear correlation of slope close to unity (Fig. 3). The results of linear regression indicate that linear correlation coefficients (r) are all circa 1. This behaviour suggests that the adsorption of PPN and TTN at the mild steel/1 M HCl interface obeys to Langmuir adsorption isotherm. The K_{ads} constant is determined from the intercept in Fig. 3 according to the following assumptions:

- That the inhibitors form a mono (molecule) layer on the iron surface at the maximum inhibition of corrosion weight loss;
- That there is no interaction between the adsorbed species on the electrode surface [23];
- That PPN and TTN are adsorbed on the iron surface according to the equations:



Thus, the values of K_{ads} for the two studied inhibitors, used at different temperatures, are presented in Table 2.

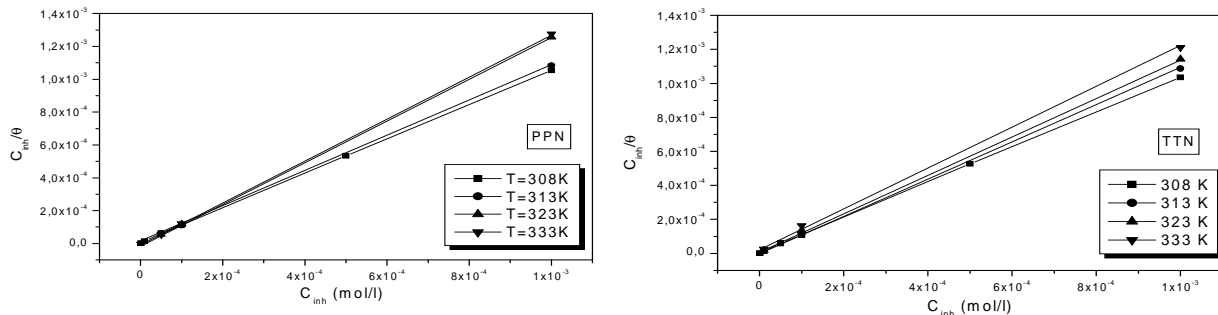


Fig. 3: Langmuir isotherm adsorption (C_{inh}/θ vs. C_{inh}) of both inhibitors derived from weight loss measurements at 25°C

According to Vant Hoff equation:

$$\ln K_{ads} = -\frac{\Delta_{ads}H}{RT} + cte$$
(6)

Then, the adsorption heat can be calculated approximately as follows:

$$\Delta_{ads}H = R \frac{T_1 T_2}{T_2 - T_1} \ln \left(\frac{K_2}{K_1} \right)$$
(7)

As the experiments are done at the standard pressure (~1 bar) and the solution concentration is so low that it is close to standard conditions, the adsorption heat can be approximately regarded as the standard adsorption heat $\Delta_{ads}H^\circ$. The standard free energy of adsorption $\Delta_{ads}G^\circ$ is obtained according to [24]:

$$K_{ads} = \frac{1}{55.55} e^{-\left(\frac{\Delta_{ads}G^\circ}{RT}\right)}$$
(8)

The large positive values of adsorptive equilibrium constant K_{ads} and the large negative values of the free energy of adsorption $\Delta_{ads}G^\circ$ in 1 M HCl indicate that PPN and TTN are strongly adsorbed on the mild steel surface [25] (Table 2).

Table 2: Adsorption parameters of mild steel in 1 M HCl in the presence of 10^{-3} M of PPN and TTN inhibitors at different temperatures

Inhibitors	T K	r^2	K_{ads}	slope	$\Delta_{ads}G^\circ$ kJ mol^{-1}	$\Delta_{ads}H^\circ$ kJ mol^{-1}	IE _{WL} %
TTN	308	1	212216	1.03	-41.72	-47.56	94.5
	313	1	285460	1.14	-43.17		92
	323	0.999	71101	1.12	-40.82	-63.50	87.5
	333	0.999	34968	1.18	-40.11		82.6
PPN	308	0.9997	178720	1.14	-41.28		94.9
	313	0.9999	173513	1.03	-41.88	-40.32	92.3
	323	1	116789	1.02	-42.15		90.9
	333	1	89522	1.17	-42.72	-23.78	91.5

The values of the free energy of adsorption for the two compounds are as calculated from the Langmuir-type adsorption. Generally, the values of $\Delta_{ads}G^\circ$ below -20 kJ mol^{-1} are consistent with electrostatic interaction, while those above -40 kJ mol^{-1} involve chemisorption [26]. The values of $\Delta_{ads}G^\circ$ for the two compounds point out to the spontaneity of the adsorption process under investigated experimental conditions and also stipulate that the adsorption of two compounds occur predominantly by chemisorption.

The inhibition is very good even at low concentration (Figs. 1 and 2). The adsorption equilibrium constant decreased with rise of temperature, which indicated that it is difficult to adsorb on the steel surface. It is also reported that the inhibition of PPN is good, and its inhibition efficiency is slightly temperature-independence. In contrast, the inhibition efficiency of TTN decreases with temperature (see Fig. 2). The negative values of adsorption heat $\Delta_{ads}H^\circ$ of the two inhibitors in 1M HCl show that the process of adsorption is exothermic.

3.2. Effect of temperature at 10^{-3} M of PPN and TTN

The effect of temperature on the inhibition efficiency is determined for 1 M HCl solution containing 10^{-3} M of the TTN and PPN, at different temperatures, ranging from 25 to 80 °C. The choice of this concentration is justified by the fact that at 10^{-3} M, the best inhibition efficiency is obtained at temperature 25°C. The results obtained by weight loss at various temperatures are given in Table 3.

Table 3: Corrosion parameters obtained from weight at various temperatures studied for mild steel in 1 M HCl at $10^{-3} \text{ mol L}^{-1}$ of PPN and TTN inhibitors

Inhibitors	Temperature K	W_{corr} $\text{mg cm}^{-2} \text{ h}^{-1}$	IE %
1 M HCl	298	1.76	-
	313	2.12	-
	323	3.52	-
	333	6.92	-
	343	13.38	-
	353	22.95	-
	PPN	298	0.09
313		0.16	92.4
323		0.22	93.7
333		0.59	91.4
343		1.04	92.2
353		2.07	90.9
TTN	298	0.06	96.6
	313	0.17	91.9
	323	0.44	87.5
	333	1.2	82.6
	343	3.4	74.5
	353	7.9	65.5

It is noticed that the corrosion rate increases with increasing temperature; this effect is attributed to the increased migration rate of proton H^+ with increasing temperature [27]. The inhibition efficiency is found to decrease drastically from 96.6% to 65.5% for TTN whereas for PPN the decrease is very slow and remains circa constant with increasing temperature from 25 to 80 °C. The values of the activation energy E_a are calculated from the Arrhenius equation:

$$W_{corr} = A e^{-\left(\frac{E_a}{RT}\right)} \quad (9)$$

W_{corr} is the corrosion rate, A the pre-exponential factor, T the absolute temperature and R is the universal gas constant.

The plots of logarithm of the corrosion rate W_{corr} versus reciprocal temperature are given in Figure 4.

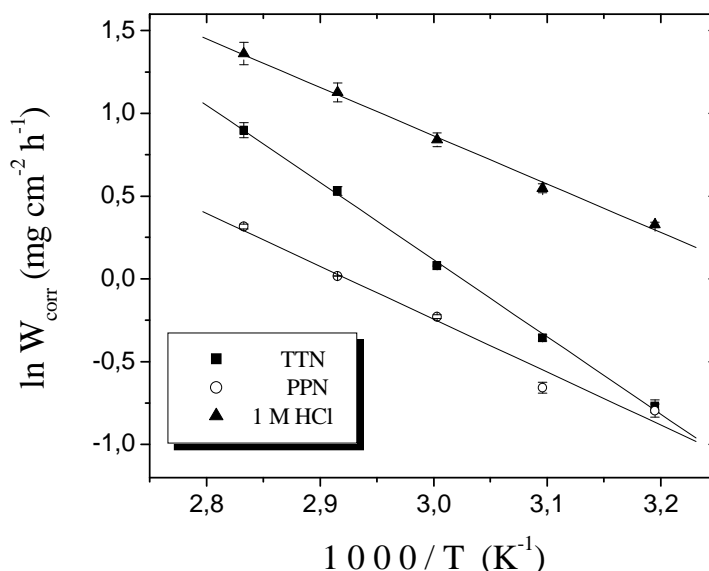


Fig. 4: Arrhenius plots of $\ln W_{corr}$ versus $1/T$ at $10^{-3} \text{ mol L}^{-1}$ of PPN and TTN inhibitors

The plots obtained are straight lines and the slope of each straight line gives its activation energy E_a . The E_a value for the corrosion of mild steel in 1M HCl, is found equal to $E_a=56.02 \text{ kJ.mol}^{-1}$ which is in agreement with the literature [28,29]. For TTN and PPN which act as effective inhibitors, the E_a values are higher and equal to $E_a = 89.33 \text{ kJ.mol}^{-1}$ and $E_a = 61.19 \text{ kJ.mol}^{-1}$ for TTN and PPN, respectively.

It is well recognized that the temperature dependence of the inhibition effect and the comparison of the values of the apparent activation energy, E_a , of the corrosion process in absence and presence of inhibitors can provide further evidence [7] concerning the mechanism of the inhibition action. The decrease of the inhibitor efficiency with increasing temperature, which refers to a higher value of E_a , when compared to free solution, is interpreted as an indication for an electrostatic character of the inhibitor's adsorption. However, the lower value of E_a in inhibited solution compared to uninhibited solution can be explained by strong chemisorption bond between the inhibitor and the metal. Some authors reported that electrostatic adsorption proceeds irrespective of the fact that the E_a value in the presence of inhibitor is lower than that in free solution [6]. Hence, the lower value of the activation energy of the corrosion process in the free inhibitor solution compared to those in inhibited media is generally attributed to the physical adsorption. Consequently, both of the studied PPN and TTN inhibitors have a character of physisorption, especially for PPN for which the chemisorption is confirmed both by the fact that the inhibiting efficiency is circa temperature independent as well as by the value of free energy of adsorption.

3.3. Polarization curves

Current-potential characteristics resulting from potentiodynamic curves for the mild steel electrode in 1 mol L^{-1} HCl in the absence and presence of the studied compounds are evaluated. Fig. 5 depicts typical potentiodynamic polarization curves of the two compounds at different concentrations.

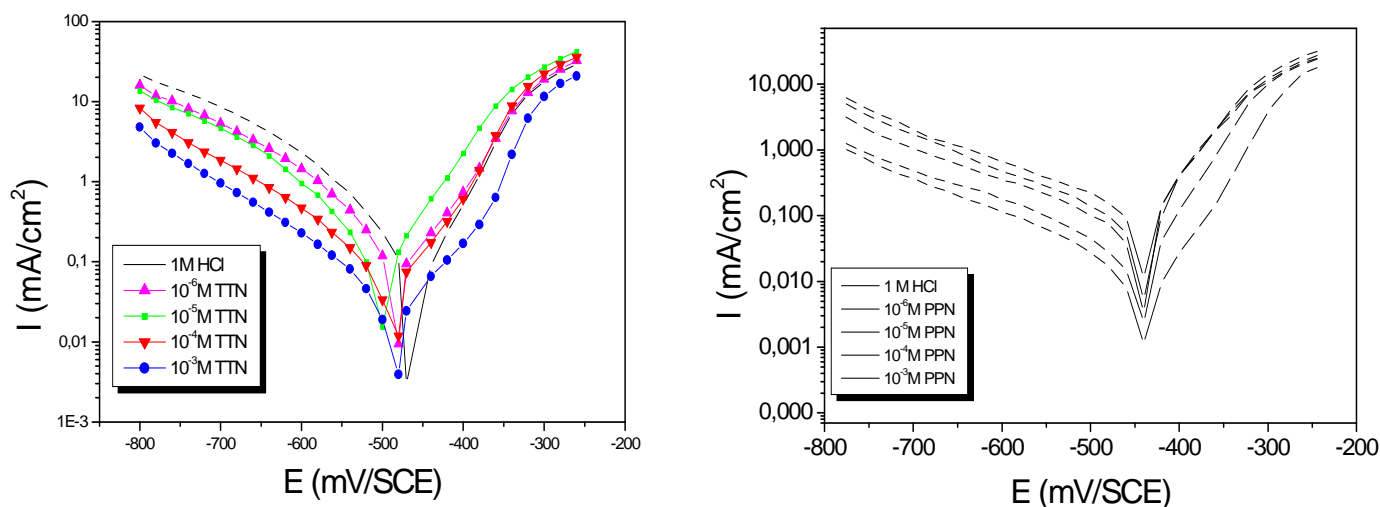


Fig.5: Polarization curves for mild steel in 1 M HCl containing different concentrations of PPN and TTN at 25 °C.

For the studied inhibitors, one notes that an increase in inhibitors concentration makes a decrease in cathodic as well as anodic current densities. Furthermore, the corrosion potential remains almost constant with inhibitors addition at different concentrations. Thus, the inhibitors under investigation are of mixed type inhibitors.

For higher overvoltage (more than -0.3 V/sce approximately), the various polarization curves tend to converge, with the high currents densities. This convergence is often explained by the fact that at high anodic potentials, the organic compounds are desorbed then the dissolution of iron takes place on an almost naked metal surface [30,31]. This interpretation is at all the more plausible since in this field of potential, all the polarization curves obtained in the presence of inhibitors approach that obtained with the blank solution.

Table 4 represents the various electrochemical parameters for mild steel corrosion in 1 M HCl containing different concentrations of the undertaken compounds.

Table 4: Polarization parameters in the corrosion of mild steel in 1 M HCl containing different concentrations of PPN and TTN at 25 °C

Inhibitors	Concentration mol L ⁻¹	E _{corr} mV _{sce}	-b _c mV dec ⁻¹	b _a mV dec ⁻¹	I _{corr} μA cm ⁻²	IE _{L-E} %
HCl	00	-439	139	75	238	-
TTN	10 ⁻⁶	-480	120	76	102	57
	10 ⁻⁵	-500	108	83	74	69
	10 ⁻⁴	-489	148	78	38	84
	10 ⁻³	-480	148	84	25	89
PPN	10 ⁻⁶	-440	146	68	185	23
	10 ⁻⁵	-441	147	69	114	52
	10 ⁻⁴	-438	148	64	68	71
	10 ⁻³	-442	145	65	31	87

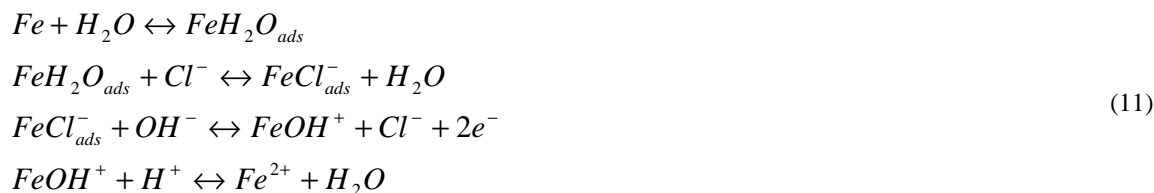
The cathodic Tafel slope (b_c), relating to the polarization of mild steel in 1 mol L⁻¹ HCl, is equal to -139 mV dec⁻¹. As it is brought back in the literature [31], this value indicates, in general, that the reduction reaction of hydrogen on iron takes place according to the mechanism of Volmer-Heyrovsky:



In the presence of PPN and TTN inhibitors, the b_c value increases, but not necessarily resulting from a modification of the reaction mechanism [32]. Indeed, when the rate of covering increases with increasing of inhibitors

concentration, the electrode active surface is reduced and the adsorbed film can have an ohmic behavior, which appears by an increase in the value of b_c [33]. The reduction reaction of hydrogen may then follow the same mechanism as in absence of inhibitor. In this case, the hydrogen adsorption on the metal surface is less than the adsorption of the inhibitor molecules. Consequently, the Heyrovsky reaction is thus limited by the small quantity of the species H_{ads} [31].

The anodic Tafel slopes (b_a), relating to the iron polarization in 1M HCl, is 75 mV.dec⁻¹. This value is in agreement with the obtained result by other studies of the iron corrosion in 1 M HCl medium [34-36]. In this case, Lorenz and al. [36] suggest a process of dissolution activated by Cl^- ions, according to the reaction pathway:



In the inhibited media, the anodic Tafel slopes remain included between 65-84 mV.dec⁻¹. Thus, although compounds PPN and TTN decrease the dissolution of iron, they do not seem to modify its mechanism; the dissolution thus being done primarily on the free face of metal [34]. The current density (I_{corr}) is determined by extrapolation of the linear slope of the cathodic or anodic curves to the corrosion potential and the inhibiting efficiency $IE_{T-E}\%$ is deduced from it.

The results, shown in Table 4, illustrate that the corrosion current density of iron in 1 M HCl is 238 μ A.cm⁻². This value is comparable with those found by other authors, under similar conditions [37]. The addition of PPN and TTN to the electrolytic solution involves a reduction in I_{corr} . This reduction is marked more and more when the concentration of each inhibitor increases until the critical concentration of 10⁻³ M for which one obtains values of 25 and 31 μ A.cm⁻² for TTN and PPN, respectively. Consequently, TTN has an inhibiting efficiency of 89%, and 87%. These results are in agreement with the values obtained by weight loss.

CONCLUSION

The following conclusions were drawn from this study:

1. The inhibition effects of 2-{bis[(5-méthyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methyl]amino} ethanol (PPN) and 3-[bis(thien-2-ylmethyl)amino]propan-1-ol (TTN) on the corrosion of mild steel in hydrochloric acid solution (1M) are investigated by weight loss and electrochemistry methods.
2. The results reveal that both products are very good mixed inhibitors at low concentration.
3. The adsorption of the studied inhibitors on the mild steel surface basically obeys the Langmuir adsorption isotherm equation.
4. The set of results from the study of temperature effect on the inhibiting efficiency, the free energy of adsorption derived from adsorption process as well as the obtained values of activation energy of the corrosion process, it is suggested that the PPN inhibitor is predominantly chemisorbed on mild steel surface while TTN is essentially physisorbed.

REFERENCES

- [1] B. Zerga, M. Sfaira, Z. Rais, M. Ebn Touhami, M. Taleb, B. Hammouti, B. Imelouane, A. Elbachiri, *Matériaux & techniques*, **2009**, 97, 297.
- [2] B. Zerga, A. Attayibat, M. Sfaira, M. Taleb, B. Hammouti, M. Ebn Touhami, S. Radi, Z. Rais, *Journal of Applied. Electrochemistry* **2010**, 40, 1575.
- [3] M.B. Cisse, B. Zerga, F. El Kalai, M. Ebn Touhami, M. Sfaira, M. Taleb, B. Hammouti, N. Benchat, S. El Kadiri, A.T. Benjelloun, *Surface Review and Letters*, **2011**, 18, 303.
- [4] B. Zerga, R. Saddik, B. Hammouti, M. Taleb, M. Sfaira, M. Ebn Touhami, S.S. Al-Deyab, N. Benchat, *International Journal of Electrochemical Science*, **2012**, 7, 631.

- [5] B. Zerga, B. Hammouti, M. Ebn Touhami, R. Tourir, M. Taleb, M. Sfaira, M. Bennajjeh, I. Forsal, *International Journal of Electrochemical Science*, **2012**, 7, 471.
- [6] S. Aloui, I. Forsal, M. Sfaira, M. Ebn Touhami, M. Taleb, M. Filali Baba, M. Daoudi, *Portugaliae Electrochimica Acta*, **2009**, 27, 599.
- [7] Y. Aouine, M. Sfaira, M. Ebn Touhami, A. Alami, B. Hammouti, M. Elbakri, A. El Hallaoui, R. Tourir, *International Journal of Electrochemical Science*, **2012**, 7, 5400.
- [8] K. Benbouya, B. Zerga, M. Sfaira, M. Taleb, M. Ebn Touhami, B. Hammouti, H. Benzeid, El M. Essassi, *International Journal of Electrochemical Science*, **2012**, 7, 6313.
- [9] K. Adardour, O. Kassou, R. Tourir, M. Ebn Touhami, H. ElKafsaoui, H. Benzeid, El M. Essassi, M. Sfaira, *Journal of Materials and Environmental Science*, **2010**, 1, 129.
- [10] Z. El Adnani, M. Mcharfi, M. Sfaira, M. Benzakour, A.T. Benjelloun, M. Ebn Touhami, B. Hammouti, M. Taleb, *International Journal of Electrochemical Science*, **2012**, 7, 6738.
- [11] Z. El Adnani, M. Mcharfi, M. Sfaira, A.T. Benjelloun, M. Benzakour, M. Ebn Touhami, B. Hammouti, M. Taleb, *International Journal of Electrochemical Science*, **2012**, 7, 3982.
- [12] S. Muralidharan, M.A. Quraishi, S.V.K. Iyer, *Corros. Sci.*, **1995**, 37, 1739.
- [13] F. Bentiss, M. Traisnel, L. Gengembre, M. Lagrenée, *Appl. Surf. Sci.*, **2000**, 161, 194.
- [14] N. Harckerma, R.M. Hurd, in: *Proceedings of the First International Congress on Metallic Corrosion*, Butterworths, London, **1962**, p. 166.
- [15] P.N.G. Shankar, K.I. Vasu, *J. Electrochem. Soc. India*, **1983**, 32, 47.
- [16] S. Radi, A. Attayibat, A. Ramdani, Y. Lekchiri, B. Hacht, M. Bacquet, M. Morcellet. *Sep. Sci. Technology*, **2007**, 42, 3493.
- [17] A. Attayibat, S. Radi, Y. Lekchiri, A. Ramdani, B. Hacht, M. Morcellet, M. Bacquet, S. Willai. *J. Chem. Res.*, **2006**, 12, 788.
- [18] F. Mansfeld, *Corrosion Mechanisms*, Marcel Dekker, New York, **1987**, p. 119.
- [19] R.J. Chin, K. Nobe, *J. Electrochem. Soc.*, **1971**, 118, 545.
- [20] T.P. Zhao, G.N. Mu, *Corrosion Science*, **1999**, 41, 1937.
- [21] G.N. Mu, T.P. Zhao, M. Liu, T. Gu, *Corrosion*, **1996**, 52, 853.
- [22] J. Bard Allen, *Electrochemical Methods*, John Wiley Sons, **1980**, p. 517.
- [23] E. Khamis, *Corrosion*, **1990**, 46, 478.
- [24] M. Elachouri, M.S. Haiji, *Corrosion*, **1996**, 52, 103.
- [25] M.A. Quraishi, J. Rawat, M. Ajmal, *Journal of Applied Electrochemistry*, **2000**, 30, 745.
- [26] Y. Gonzalez, M.C. Lafont, N. Pébère, G. Chatainier, J. Roy, T. Bouissou, *Corros. Sci.*, **1995**, 37, 1823.
- [27] M.N. Desai, M. B. Desai, *Corros. Sci.*, **1984**, 24, 649.
- [28] M.N. Desai, M. B. Desai, C.B. Shah, S.M. Desai, *Corros. Sci.*, **1986**, 26, 827.
- [29] G.K. Gomma, *Mater. Chem. Phys.*, **1998**, 55, 131.
- [30] E. Laengle, N. Hackerman, *J. Electrochem. Soc.*, **1971**, 118, 1273.
- [31] K.C. Pillai, R. Narayan, *Corros. Sci.*, **1983**, 23, 151.
- [32] A.K. Vijh, B.E. Conway, *Chem. Rev.*, **1967**, 67, 623.
- [33] E. Mc.Cafferty, N. Hackerman, *J. Electrochem. Soc.*, **1972**, 119, 146.
- [34] T.A. Oftedal, *Electrochim. Acta*, **1973**, 18, 401.
- [35] W.J. Lorenz, H. Yamaoka, H. Fisher, *Phys. Chem.* **1963**, 67, 932.
- [36] L. Meszaros, B. Lengyel, A. Frignani, C. Moticelli, G. Trabaneli, *Mater. Chem. Phys.*, **1985**, 12, 189.
- [37] G. Perboni, G. Rocchini, *Proceedings of the 10th international congress on metallic corrosion (Madras)*, **1987**, p.2723.