

INVESTIGATION OF THE INHIBITIVE EFFECT OF PYRAZOLO [3, 4-B] PYRIDINE ON CORROSION OF STAINLESS STEEL IN 1 M HCl SOLUTIONS

M.A. El Mhammedi¹, S. Fadel², A. Chtaini^{1*},
E.M. Rakib², M. Khouili²

¹*Laboratoire d'Electrochimie et de Bio corrosion, Faculté des Sciences
et Techniques, Université Cadi Ayad, BP : 523, Beni Mellal, Maroc*

²*Laboratoire de Chimie Organique et Analytique, Faculté des Sciences
et Techniques, Université Cadi Ayad, BP : 523, Beni Mellal, Maroc*

*Corresponding author: chtainia@yahoo.fr, Fax 00 212 23 48 52 01

Received: 17/11/2005

Accepted after revision: 17/02/2006

Abstract: The purpose of this study to investigate the effect of pyrazolo [3-4-b] pyridine on the corrosion inhibition of stainless steel in 1.0M hydrochloric acid (HCl) by using weight loss method, potentiodynamic polarization methods, and electrochemical impedance spectroscopy.

It was found that the adsorption of inhibitor could prevent steel from weight loss and the adsorption accorded with the Langmuir adsorption, the corrosion protection could be explained by the adsorption of inhibitor and formation of a protective layer attached to the metal surface.

Keywords: *pyrazolo [3-4-b] pyridine, corrosion inhibition, adsorption, stainless steel*

INTRODUCTION

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1].

Hydrochloric acid solutions are widely used for the pickling, cleaning, descaling etching of stainless steel. The dissolution rate of the metal is quite high and the inhibition of these solutions with organic compounds, which may retard the dissolution rate, is favored. Different compounds have been reported to inhibit the corrosion of stainless steel. Most of the well known acid inhibitors are organic compounds containing N, O atoms [2–6].

The corrosion inhibition of stainless steel by different inhibitors in acidic environments has been studied by several authors [7–11]. It has been reported that the adsorption of nitrogenous compounds occurs with aromatic rings parallel to the metal surface [12].

The synthesis of new organic molecules offers various molecular structures containing several heteroatoms and substituents. Their adsorption is generally explained by the formation of an adsorptive film of a physical or chemical character on the metal surface. In continuation of our work on development of organic compounds as acid inhibitors, we have chosen an organic inhibitor namely pyrazolo [3-4-b] pyridine A (Fig. 1) with a view to study its inhibiting properties on corrosion of steel in 1.0M HCl.

In the present work, we investigate the corrosion of steel in 1.0 M HCl by inhibitor. Weight loss tests and electrochemical techniques (potentiodynamic and R_p polarization and impedance measurements) have been used to study the effect of addition of this compound on the corrosion of steel in hydrochloric acid solution.

EXPERIMENTAL

The inhibitor was synthesized by a previously described procedure [13]. The molecular structures are shown in Fig. 1.

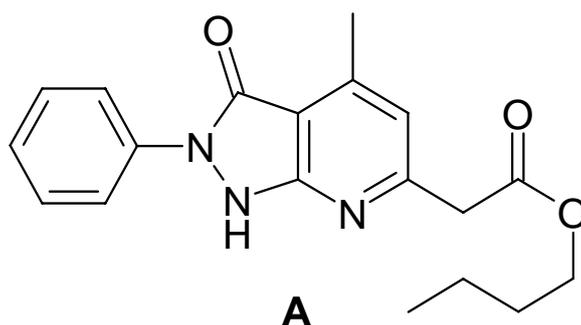


Figure 1. Molecular formulae of 2-(4-Methyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazolo [3,4-b] pyridin-4-yl) acetic acid butyl ester

The aggressive solution (1 M HCl) was prepared by dilution of analytical grade 36% HCl with bidistilled water. The solutions were prepared by mixing HCl with the inhibitor.

All tests have been performed in deaerated solutions and at room temperature (25°C). For electrochemical measurements, a conventional three-electrode glass cell with a

platinum flat (1cm x 1cm) counter-electrode a saturated calomel electrode (SCE) as reference and Stainless steel as working electrode connected to a Voltalab 10 type computer controlled potentiostat. The working electrode surface (1cm²) mechanicals polished with emery paper cleaned with distilled water and finally dried with filter paper.

The electrochemical analysis involved, measuring of open circuit potential, gravimetric measurements, polarization studies and AC impedance in acidic media 1M (HCl).

RESULTS AND DISCUSSIONS

The open circuit potentials of the stainless steel in 1M HCl with and without inhibitor solution are shown in Fig. 2. With inhibitor the potential stabilized after 20 min at 0.5 V. The polarization curves for steel in hydrochloric acid at various concentrations of inhibitor are shown in Fig. 3.

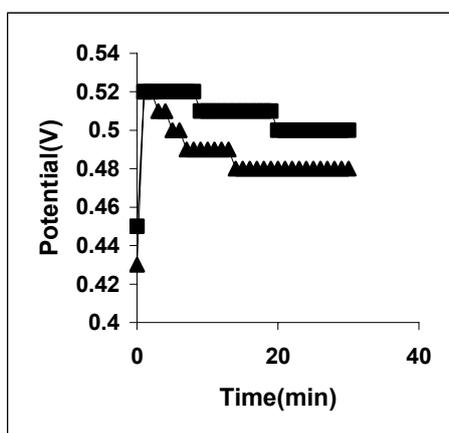


Figure 2. Open-circuit potential vs. time of the stainless steel in 1.0 M HCl solution: (▲) without inhibitor, (■) with 20 mg/L of inhibitor

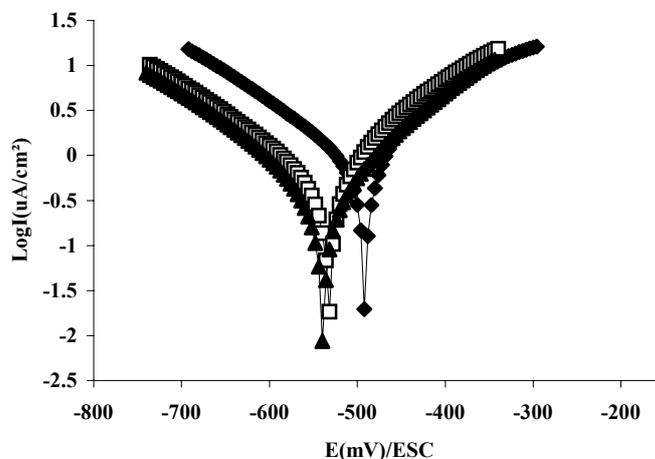


Figure 3. Polarization curves of stainless steel in 1 M HCl with and without inhibitor at different concentrations. (◆) Reference, (□) 20 mg/L, (▲) 60 mg/L.

The electrochemical parameters determined from the polarization curves are given in Table 1.

Table 1. Electrochemical parameters from polarization measurements on stainless steel in 1 M HCl without and with different inhibitor concentrations

Electrodes	Reference	20 mg (inh)	60 mg (inh)
E (i=0) (mV)	-492.1	-533.4	-539.3
R _p (Ω.cm ²)	28.36	47.75	72.47
J _{corr.} (mA/cm ²)	0.728	0.464	0.416
B _a (mV/dec)	104.5	107.7	131.1
B _c (mV/dec)	-145.8	-145.9	-150.2

The corrosion behaviour of stainless steel, in acidic media with and without inhibitor concentration was investigated by the ESC method at room temperature (Fig. 4). The charge transfer resistance is calculated from the difference in impedance at lower and higher frequencies.

The parameters derived from these investigations are given in Table 2. It was found that, as the inhibitor concentration increases, the R_t increase, but the C_{dl} values tend to decrease, the decrease in the C_{dl} values is due to the adsorption of inhibitor on the metal surface.

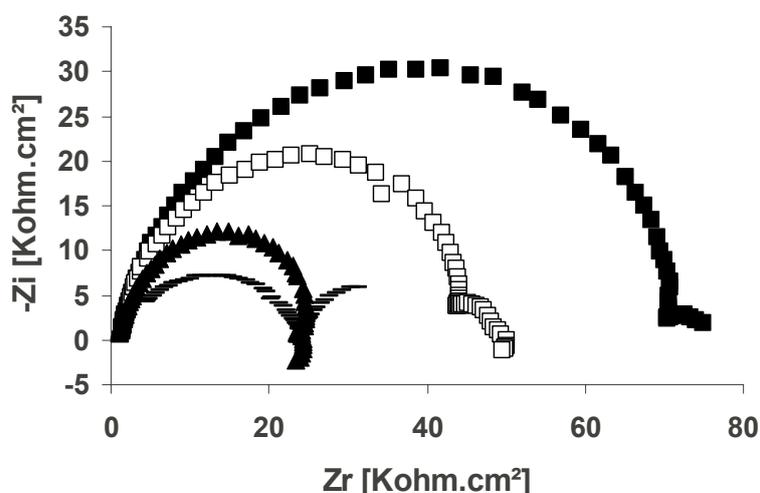


Figure 4. Electrochemical impedance spectra of steel in 1 M HCl with and without different inhibitor concentrations:

(-) Reference, (▲) 20 mg/L, (□) 40 mg/L, (■) 80 mg/L.

Table 2. Nyquist diagrams for stainless steel in 1 M HCl containing different concentrations of inhibitor

Inhibitor	Reference	20 mg/L	40 mg/L	80 mg/L
R1 (Ω.cm ²)	0.833	1.226	1.859	1.411
R2 (Ω.cm ²)	15.61	25.01	44.35	72.14
C (μF/cm ²)	57.8	402.1	452.1	348.5

The weight loss of steel in acidic media without and with inhibitor is determined after 30 h of immersion, the inhibition efficiency of inhibitor for the corrosion of stainless steel was calculated by using the following equation:

$$E[\%] = \left[1 - \frac{W_{corr(inh)}}{W_{corr}} \right] \times 100$$

where w_{corr} and $w_{corr(inh)}$ are the weight loss for steel after immersion in acidic media without and in the presence of various concentration of inhibitor. The parameters derived from this investigation are given in Table 3 and Fig. 5.

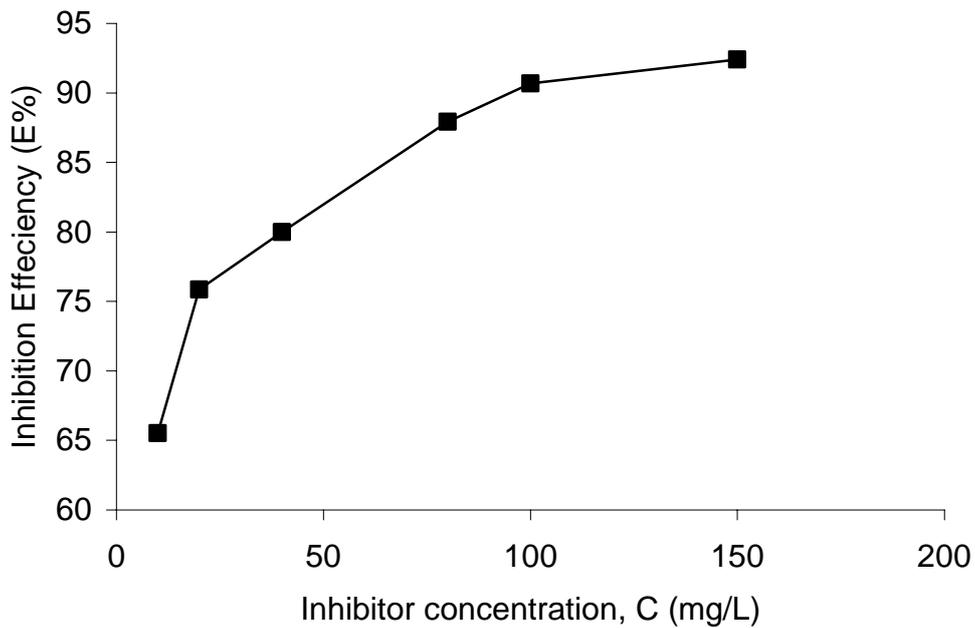


Figure 5. Inhibition efficiency for stainless steel in 1M HCl containing different inhibitor concentrations at room temperature

Table 3. Inhibition efficiency obtained from the weight loss for different concentration of inhibitor in 1 M HCl

Concentration of inhibitor [mg/L]	Corrosion rate [mg/(cm ² h)]	Inhibition efficiency [E %]
0	2.9	-
10	1	65.51
20	0.7	75.86
40	0.58	80.00
80	0.35	87.93
100	0.27	90.68
150	0.22	92.41

It is clear that inhibition efficiency increased with increasing inhibitor concentrations. The corrosion inhibition was caused by the adsorption of inhibitor on the metal surface in 1 M HCl; the degree of surface coverage (θ) for inhibitor in acidic media was evaluated from weight loss measurements using the relation [14]:

$$\theta = \frac{(w_0 - w)}{(w_0 - w_m)}$$

where w_m is the smallest weight loss.

Table 4 summarizes the values of θ of stainless steel in the presence of various concentrations of inhibitor at room temperature.

Table 4. Values of coverage obtained from the weight loss for different concentrations of inhibitor in 1 M HCl at room temperature

Inhibitor conc. [mg/L]	0	10	20	40	80	100	150
Coverage [θ]	0.00	0.70	0.82	0.86	0.95	0.98	1.00
C/ θ	-	14.28	24.39	46.51	84.21	102	150

The values of θ increased with increasing inhibitor concentrations.

The Langmuir isotherm was applied to investigate the adsorption mechanism by the following expression [15, 16]:

$$\theta = \frac{K \cdot C}{1 + K \cdot C} \Leftrightarrow \frac{C}{\theta} = \frac{1}{K} + C \quad (\theta \neq 0)$$

where C is the inhibitor concentration and K is defined as [17]:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

C/ θ versus inhibitor concentration at room temperature is shown in Fig. 6. The linear regression between C/ θ and C was calculated, and K and ΔG_{ads} can be calculated according to the above equations. The result was shown in Table 5.

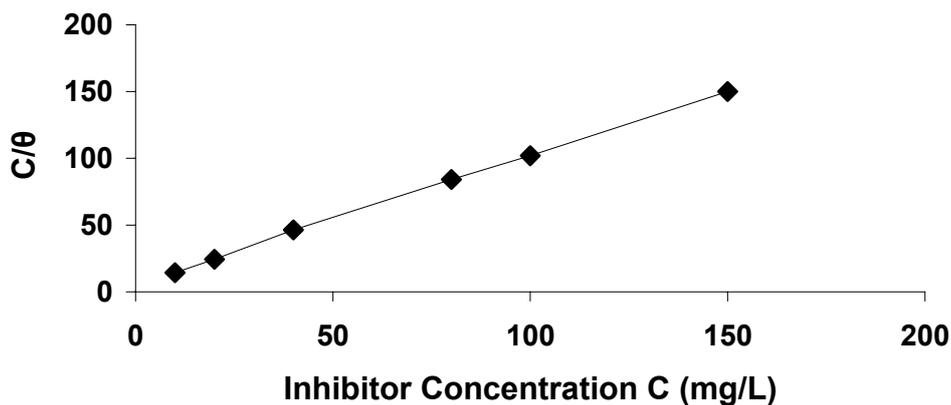


Figure 6. The relation between C/ θ (mg/L) and C (mg/L) at room temperature

Table 5. Adsorption parameters of inhibitor on the steel surface at 25 °C

Linear correlation coefficient	K	ΔG_{ads} [kJ/mol]
0.969	4.5	13.678

It can be found that the correlation coefficients of straight line C/θ versus C of inhibitor approaches 1 at room temperature. This illustrates that the aforementioned supposition is tenable on the whole, that is, the adsorption of inhibitor on steel surfaces conforms to Langmuir's adsorption isothermal equation.

The SEM images shown in Fig. 7 provide an explanation for the phenomena. It is clear that the plate of stainless steel is uniformly covered with the protecting film. This observation clearly proved that the inhibition is due to the formation of an insoluble barrier film on the stainless steel surface.

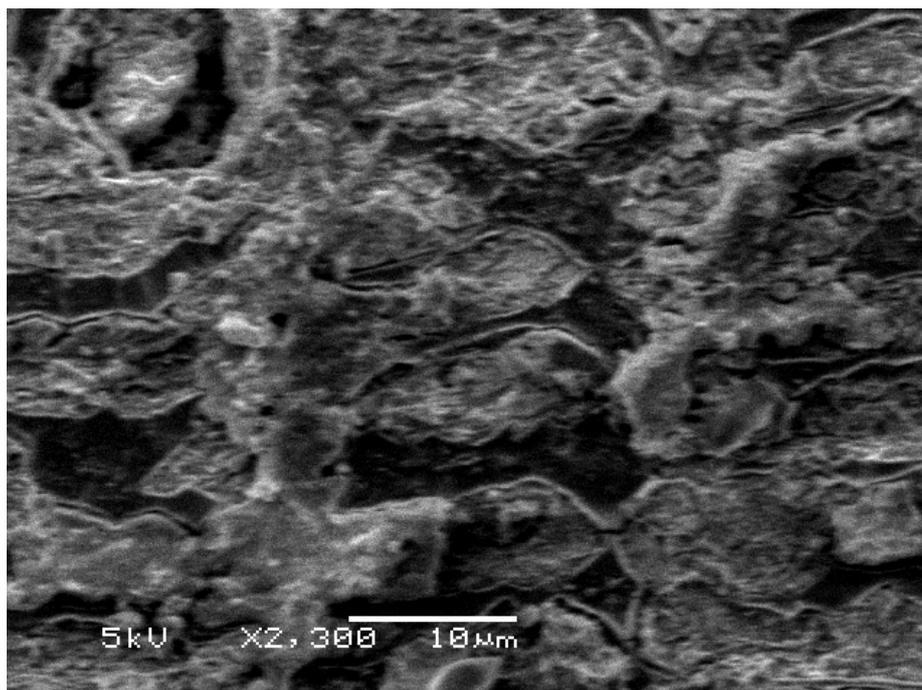


Figure 7. SEM photographs of the surface for stainless steel after immersion at 25 °C in 1 M HCl

CONCLUSION

All investigated pyrazolo [3-4-b] pyridine A have shown good inhibiting properties for stainless steel corrosion in 1 M hydrochloric acid (HCl).

Adsorption mechanism of inhibitor on the stainless steel surface in 1.0M hydrochloric acid (HCl) was investigated, assuming the decrease of the weight loss of stainless steel was caused by the adsorption of inhibitor on the steel surface and obeys the Langmuir equation.

REFERENCES

1. Trabnelli, G., *Corrosion*, **1991**, 47, 410.
2. Raicheva, S.N., Aleksiev, B.V., Sokolova, E.I.: *Corros. Sci.*, **1993**, 34, 343.
3. Hluchan, V., Wheeler, B.L., Hackerman, N., *Werkst. Korros.*, **1998**, 39, 512.

4. Schweinsberg, D.P., Ashworth, V.: *Corros. Sci.*, **1988**, 28, 539.
5. Cheng, X.L., Ma, H.Y., Chen, S.H., Yu, R., Chen, X., Yao, Z.M.: *Corros. Sci.*, **1999**, 41, 321.
6. Bouayed, M., Rabaa, H., Schiri, A., Saillard, J.-Y., Ben Bachir, A., Le Beuze, A.: *Corros. Sci.*, **1999**, 41, 501.
7. Vosta, J., Pelikanj, S.M.: *Werkst. Korros.*, **1974**, 25, 750.
8. Sathiyarayanan, S., Dhawan, S.K., Trivedi, D.C., Balakrishnan, K.: *Corros. Sci.*, **1992**, 33, 1831.
9. Zvauya, R., Dawson, J.L.: *J. Appl. Electrochem.*, **1994**, 24, 943.
10. Mohamed, A.K., Abd El-Masoud, S.A., Fouda, A.S.: *Bull. Soc. Chim. Belg.*, **1996**, 105, 363.
11. Aksut, A.A., Onal, A.N.: *Corros. Sci.*, **1997**, 39, 761.
12. Schmitt, G., Bedbur, K.: *Proc. 9th International Congress on Metallic Corrosion*, Toronto, Canada, **1984**, 112.
13. Fadel, S., Hajbi, Y., Rakib, E.M., Khouili, M., Pujol, M.D., Guillaumet, G.: *Synth. Commun.*, **2004**, 34(12), 2195.
14. Sekine, I., Hirakawa, Y.: *Corrosion*, **1986**, 42, 272.
15. Zhao, T.P., Mu, G.N.: *Corros. Sci.*, **1999**, 41, 1937.
16. Mu, G.N., Zhao, T.P., Liu, M., Gu, T.: *Corrosion*, **1996**, 52, 853.
17. Khamis, E.: *Corrosion*, **1990**, 46, 476.