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# Evaluation of the inhibitor effect of new class triazole derivatives on the corrosion of ordinary steel in hydrochloric acid solution

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## ABSTRACT

*The corrosion inhibition properties of a new class of triazole derivatives, namely* **(***RS) – 2 – (2, 4 dichlorophenyl) 1 – (1H) – 1, 2, 4 triazol 1 – yl) hexane 2 OL (Hexaconazole) and 1 – ((4 – Bromo – 2 – (2, 4 –dichlorophenyle tetra hydro- 2 – furanyle) methyl) – 1 H – 1, 2, 4, - triazole (Bromuconazole***)** *on ordinary steel in 1M HCl medium were investigated using electrochemical impedance spectroscopy (EIS), potentiodynamic polarisation and weight loss measurements. The obtained results showed that these compounds are excellent inhibitors for ordinary steel in hydrochloric acid solution 1M and that the protection efficiency increases with increasing inhibitors concentration. Leading to the formation of a protective layer with a greater polarization resistance. The effect of temperature on the corrosion behaviour ordinary steel in acid solution with addition of* $10^{-3}$ *mol/l of Hexaconazole and addition of* $10^{-3}$ *mol/l of Bromuconazole were studied in the temperature range from 25C° to 50C°. Adsorption of Hexaconazole on the steel surface obeys to the Langmuir's isotherm. And adsorption of Bromuconazole on the steel surface obeys to the Temkin's isotherm. The apparent activation energies are calculated and discussed.*
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**Keywords**: Corrosion, ordinary steel, EIS, Polarization, Triazole, Inhibition, Adsorption, Hydrochloric acid.

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## INTRODUCTION

Carbon steel has been widely used as tubing material for condensers and heat exchangers in various cooling water systems because of their resistance to corrosion. Ordinary steel materials are extensively used to fabricate structures and components exposed to sea water and petroleum production and refining [1-5].

One of the most important methods in corrosion protection is the utilization of organic inhibitors. In general, the organic compounds have demonstrated a great effectiveness in inhibiting the aqueous corrosion of many metals and alloys [6-11].The inhibiting action of those organic compounds is usually attributed to interactions with metallic surface by adsorption. The adsorption of inhibitors takes place through heteroatoms such as oxygen, phosphorus and sulphur or aromatic rings containing polar groups and π electrons [12].

Subsisted triazole has desirable characteristic for a corrosion inhibitor. It has been extensively studied in several media and for different metals and alloys [13-14].

In this paper, we have studied the effect of the addition of 1,2,4-triazoles derivatives on the corrosion inhibition of ordinary steel in HCl 1M medium using electrochemical impedance spectroscopy (EIS), potentiodynamic polarisation and weight loss measurements. The thermodynamic data of adsorption and activation are determined and discussed.

## MATERIALS AND METHODS

### *2.1. Specimens*

Ordinary steel specimens containing 0.11% C , 0.24 % Si , 0.47% Mn , 0.12% Cr , 0.02% Mo , 0.1% Ni , 0.03% Al , Co< 0.0012% ,Cu 0.14% ,V < 0.003% , W 0.06% and the remainder Fe was used as the substrate. For the gravimetric and electrochemical measurements, these steel specimens were mechanically cut into 1cm × 5 cm × 0.06 cm dimensions for weight loss experiment. For electrochemical experiments. The specimens were exposed a geometrical surface area of $1cm^2$ to the electrolyte. Prior to all measurements. The specimens were mechanically polished on wet SiC paper (grade 400 – 600 - 1200), rinsed with doubly distilled water, degreased ultrasonically in ethanol for 5 min and dried with hot air.

### *2.2. Inhibitors*

### *2.2.1. Hexaconazole*

The organic compounds (Hexaconazole), used as corrosion inhibitor, is a commercial product “Anvil”.

- Brute Formula: $C_{14} H_{17} CL_2 N_3O$
- Developer Formula: **(**RS) – 2 – (2, 4 dichlorophenyl) 1 – (1 H) – 1, 2, 4 triazol 1 – Y L) Hexane 2 OL.

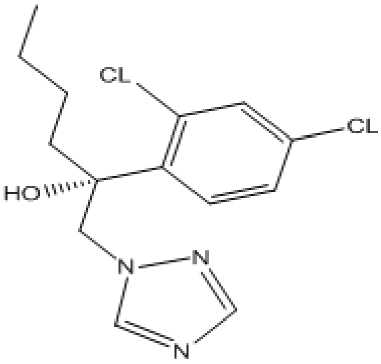

**Fig.1: the molecular formula of Hexaconazole**

### *2.2.2. Bromuconazole*

The organic compounds (Bromuconazole), used as corrosion inhibitor, is a commercial product “Vectra”.

- Brute Formula $C_{13} H_{12} BrCl_2 N_3 O$
- Developer Formula: 1- ((2 RS, 4 RS: 2 RS, 4 RS) – 4 – Bromo – 2 – (2, 4 – dichlorophenyle) tetrahydrofurfuryle) 1 H – 1, 2, 4 – triazole .1 – ((4 – Bromo – 2 – (2, 4 – dichlorophenyle tetra hydro- 2 – furanyle) methyl) – 1 H – 1, 2, 4, - triazole.

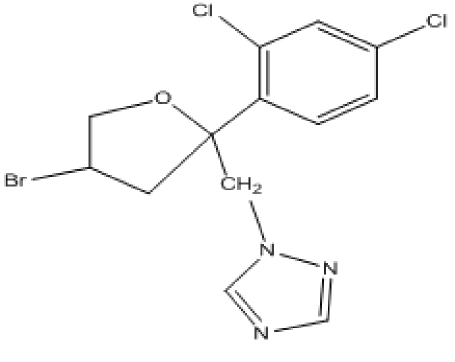

**Fig.2: the molecular formula of Bromuconazole**

### *2.3. Electrolytes*

The aggressive solutions of 1M HCL were prepared by dilution of analytical grade 37% with doubly distilled water. The concentration range of inhibition employed was varied from $10^{-5}$ M to $10^{-2}$ M in 1M HCL. And the electrolyte used was 100 ml.

### *2.4. Methods*

### *2.4.1. Gravimetric measurement:*

The weight loss of steel with and without the addition of different concentration of inhibitor was determined after immersion in simulated cooling water over 24 h at 32 C° in 100 ml, controlled thermostatically, and under air atmosphere. At the end of experiments, the specimens were cleaned and reweighed up to 10−4 g for determining corrosion rate [15].

The percentage inhibition efficiency (η%) was calculated from:

$$\eta\% = \frac{W_\circ - W}{W_\circ} \qquad \boxed{(1)}$$

Where$W_0$ and W are the values of the corrosion weight loss of steel after immersion in solutions without and with inhibitor respectively.

### *2.4.2. Electrochemical measurement:*

Electrochemical experiments were conducted using impedance equipment (Voltalab model PGZ 100) and controlled with analysis software model Voltamaster 4.

A conventional three electrode cylindrical glass and thermostated cell. The working electrode was an ordinary steel with surface area of $1cm^2$.a platinum plate of surface area of 2 $cm^2$ as the auxiliary electrode (CE) and $Hg/Hg_2Cl_2/KCl$ saturated (SCE) were used as the reference electrodes, The working electrode was immersed in test solution for 30 min until a steady state open circuit potential (Eocp) was obtained. The impedance measurements (EIS) were carried-out at Ecorr after immersion in a solution without bubbling, After the determination of steadystate current at a given potential, sine wave voltage (10 mV) peak to peak, at the frequencies between 100 KHz and 10 mHz was superimposed on the open circuit potential. The impedance diagrams are given in the Nyquist representation. Values of Rp and $C_{dl}$ were obtained from Nyquist plots. For polarisation curves, Potentiodynamic polarisation studies were performed with a scan rate of $1mv.s-^{1}$ in the potential range from -750 mV to +100 mV relative to the corrosion potential. The polarization curves were corrected for the ohmique drop measured by electrochemical impedance spectroscopy.

## RESULTS AND DISCUSSION

### *3.1. Weight loss measurement:*

The effect of addition of 1,2,4 triazole derivatives tested at different concentrations on the corrosion of ordinary steel in 1M HCl solution was studied by weight loss method at 30°C after 24 h of immersion period. The corrosion parameters such as corrosion rate (W) and inhibition efficiency E (%) are summarized in Table 1.The results showed that the corrosion rate of ordinary steel decreased whereas the inhibition efficiency increased with increasing inhibitor concentration. The maximum E (%) of each inhibitor was achieved at 10-3M and a further increase in concentration showed only a marginal change in the in the performance of the inhibitor. Hence, the optimum levels of concentrations of the inhibitors were found to be 10-3M. This behavior could be attributed to the increase of the surface area covered with adsorbed molecules of inhibitor as its concentration increases. Among the inhibitors studied; Hexaconazole performs better than that of Bromuconazole. It is generally assumed that the inhibitor adsorption onto the metal/solution interface is the first step in the mechanism of inhibition in aggressive media. 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) [16].

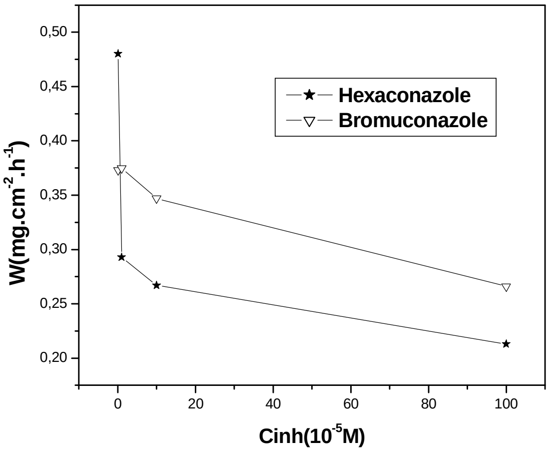

**Fig.3: Variation of corrosion rate for various concentrations of triazole derivatives in 1 M HCl at 25C°**

**Table.1: Corrosion rate of ordinary steel and inhibition efficiency for various concentrations of triazole derivatives in the corrosion of ordinary steel in 1 M HCl obtained from weight loss measurements**

| inhibitors | Concentration (M) | W (mg/cm$^2$.h) | E% |
|---|---|---|---|
| Blank | - | 2.670 | - |
| Hexaconazole | 10-6 | 0.480 | 82 |
| | 10-5 | 0.293 | 89 |
| | 10-4 | 0.267 | 90 |
| | 10-3 | 0.213 | 92 |
| Bromuconazole | 10-6 | 0.378 | 85 |
| | 10-5 | 0.375 | 86 |
| | 10-4 | 0.347 | 87 |
| | 10-3 | 0.266 | 90 |

*3.2. Potentiodynamic polarisation studies*

The cathodic and anodic polarization curves of ordinary steel with varying concentrations of Hexaconazole and Bromuconazole are shown in figs 4, 5. The deduced electrochemical parameters and inhibition efficiencies (E %) are given in Table 2. The inhibition efficiency (E %) of the inhibitors for the corrosion of steel was calculated by using corrosion current density as follows:

$$E\% = \frac{i^{\circ}_{corr} - i_{corr}}{i^{\circ}_{corr}} \qquad (2)$$

Where $i^{\circ}_{corr}$ and $i_{corr}$ are the corrosion current density values without and with the inhibitor, respectively. Determined by extrapolation of cathodic Tafel lines to the corrosion potential. It is evident the results that the addition of inhibitor caused a decrease of the current density and the cathodic and anodic curves were shifted toward positive potential region. The $E_{corr}$ values were marginally shifted in the presence Hexaconazole and Bromuconazole. The values of the corrosion current ($i_{corr}$) of ordinary steel in the inhibited solution were smaller than those for the inhibitor free solution. This observation clearly indicated that the inhibitors control the anodic and cathodic reactions and thus act as mixed type inhibitors. Cathodic current potential curves gave rise to parallel Tafel lines indicating that the hydrogen evolution is activation controlled [17]. The values of inhibition efficiency increase with increasing concentration of inhibitor. The corrosion rate in blank solution was found to be 325µA/cm$^2$ and it was minimized by adding the inhibitors to a lower value of 55 and 49 µA/cm$^2$ for ordinary steel due to adsorption of Hexaconazole and Bromuconazole on the metal surface respectively.

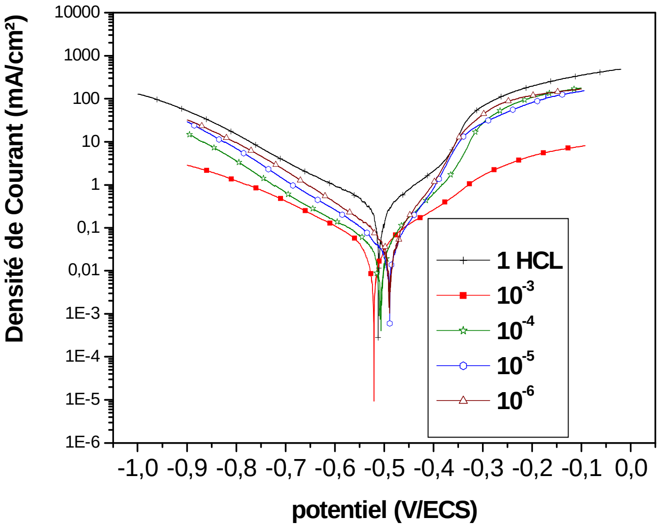

**Fig.4: Polarization curves of ordinary steel in 1M HCL containing various concentrations of Hexaconazole**

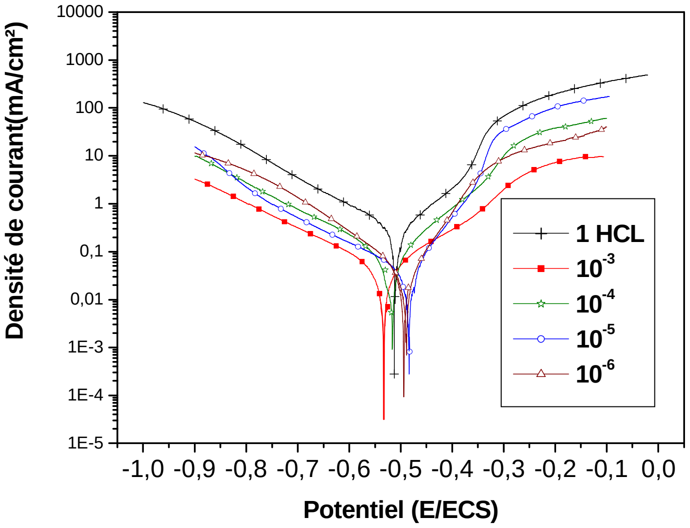

**Fig.5: Polarization curves of ordinary steel in 1M HCL containing various concentrations of Bromuconazole**

**Table.2. Electrochemical parameters of steel at various concentrations of Hexaconazole and Bromuconazole studied in 1M HCl at 25C°**

| Inhibitor | Concentration (M) | Ecorr (mv/ECS) | Icorr(mAcm$^2$) | bc | Efficacité% |
|---|---|---|---|---|---|
| Blank | - | -511 | 0.325 | -100.2 | - |
| Hexaconazole | 10-6 | -488 | 0.055 | -135 | 83 |
| | 10-5 | -489 | 0.036 | -155 | 89 |
| | 10-4 | -507 | 0.034 | -164 | 90 |
| | 10-3 | -520 | 0.025 | -170 | 92 |
| Bromuconazole | 10-6 | -493 | 0.049 | -134 | 85 |
| | 10-5 | -484 | 0.047 | -141 | 86 |
| | 10-4 | -515 | 0.044 | -142 | 86 |
| | 10-3 | -532 | 0.034 | -139 | 90 |

### *3.3. Electrochemical impedance spectroscopy (EIS)*

The corrosion behaviour of steel in hydrochloric acidic solution 1M was investigated by the ac impedance method at room temperature (30 C°) after 30 min of immersion Nyquist plots of steel in inhibited and uninhibited acidic solution various concentrations of Hexaconazole and Bromuconazole are shown in figures 6, 7. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion[18-20]. The polarization resistance values ($R_p$) are calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance ($C_{dl}$), the frequency at wich the imaginary component of the impedance is (-Zmax) is found and $C_{dl}$ values are obtained from the equation:

$$f(-Z\max)=\frac{1}{2\Pi RtCdl} \qquad \boxed{(3)}$$

The inhibition efficiency is calculated by polarisation resistance as follows

$$\eta\%=\frac{Rp-Rp\circ}{Rp} \qquad \boxed{(4)}$$

Where Rp and Rp° are the polarization resistances with and without inhibitor for ordinary steel in 1M HCl, respectively.

The impedance parameters derived from these investigations are given in table 3. It is found that the Rp values increased in the presence of inhibitors, whereas $C_{dl}$ found to be decreased. The decrease in $C_{dl}$ values was due to the adsorption of Hexaconazole and Bromuconazole on the metal surface [21]. Leading to the formation of film from acidic solution [ 22].

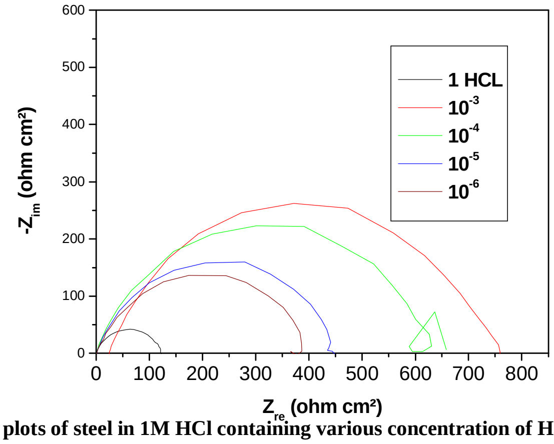

**Fig.6: Nyquist plots of steel in 1M HCl containing various concentration of Hexaconazole**

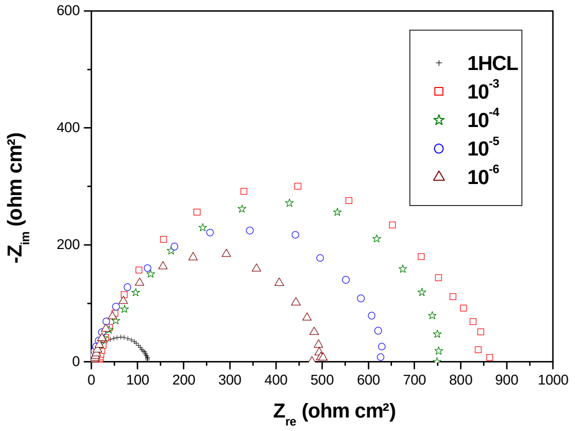

**Fig.7: Nyquist plots of steel in 1M HCl containing various concentration of Bromuconazole**

**Table.3: EIS parameters of steel at various concentrations of Hexaconazole and Bromuconazole studied in 1 M HCl at 30C°**

| Inhibitor | Concentration (M) | Rp(Ω.cm$^2$) | f max(Hz) | Cdl(µF.cm$^2$) | Efficacite% |
|---|---|---|---|---|---|
| Blank | - | 119 | 6.32 | | - |
| Hexaconazole | 10-6 | 391 | 6.32 | 60.30 | 70 |
| | 10-5 | 445 | 4 | 56.25 | 73 |
| | 10-4 | 640 | 6.32 | 40.05 | 81 |
| | 10-3 | 758 | 6.32 | 34.87 | 84 |
| Bromuconazole | 10-6 | 500 | 4 | 50.37 | 76 |
| | 10-5 | 630 | 6.32 | 24.90 | 81 |
| | 10-4 | 763 | 6.32 | 20.08 | 84 |
| | 10-3 | 866 | 6.32 | 19.12 | 86 |

### *3.4. Effect of temperature*

To study the effect of temperature on the inhibition efficiencies of Hexaconazole and Bromuconazole, polarization experiments were conducted in the range of 25–50C°, in the absence and presence of $10^{-3}$ M of inhibitors. Typical polarisation curves, obtained at different temperatures without and with $10^{-3}$ M of Hexaconazole and Bromuconazole are shown in Figs. 8, 10. Values of electrochemical parameters and E (%) are given in Table 4.

The effect of the temperature shows that the increase of corrosion current density is more pronounced with the rise of temperature for the blank solution. In the presence of the triazole compounds tested, $i_{corr}$ is reduced. We note that the efficiency of the Hexaconazole depend perfectly on the temperature and decreases with the rise of temperature from 25 to 50C°. Bromuconazole compounds act as an efficient inhibitor in the range of temperature studied and no variation to the corrosion potential has been found in the temperature range studied.

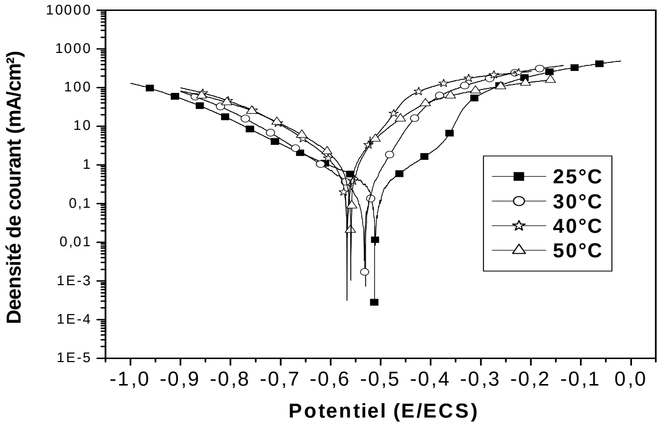

**Fig.8: Effect of temperature on the cathodic and anodic responses for ordinary steel in 1M HCl**

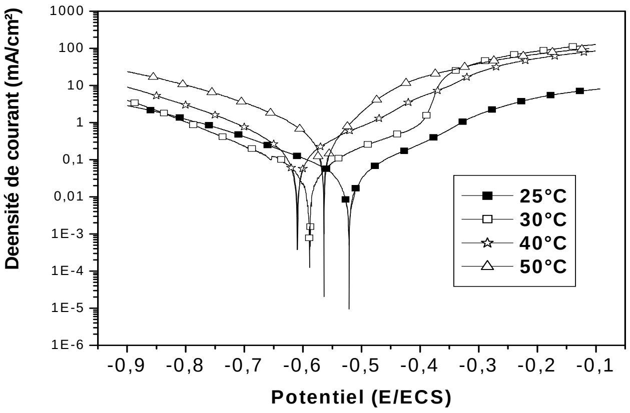

**Fig 9: Effect of temperature on the cathodic and anodic responses for ordinary steel in 1M HCl + $10^{-3}$M of Hexaconazole**

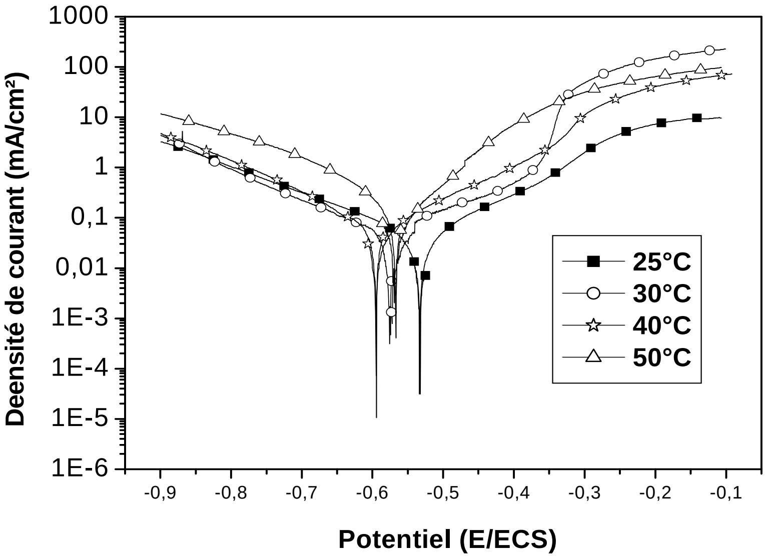

**Fig 10: Effect of temperature on the cathodic and anodic responses for ordinary steel in 1M HCl + $10^{-3}$M of Bromuconazole**

**Table.4: The influence of temperature on the electrochemical parameters for ordinary steel electrode immersed in 1M HCl without and with inhibitors**

| Inhibitor | Temperature (C°) | Ecorr (mV/ECS) | $I_{corr}$ (mA.cm$^{-2}$) | Efficacité% |
|---|---|---|---|---|
| Blank | 25 | -511 | 0.325 | - |
| | 30 | -532 | 0.370 | - |
| | 40 | -568 | 0.691 | - |
| | 50 | -559 | 1.310 | - |
| 10-3 M Hexaconazole | 25 | -520 | 0.025 | 92 |
| | 30 | -588 | 0.057 | 85 |
| | 40 | -609 | 0.142 | 79 |
| | 50 | -563 | 0.48 | 64 |
| 10-3 M Bromuconazole | 25 | -532 | 0.034 | 90 |
| | 30 | -576 | 0.047 | 87 |
| | 40 | -594 | 0.057 | 91 |
| | 50 | -565 | 0.103 | 92 |

### *3.5. Adsorption isotherm and thermodynamic parameters*

The adsorption isotherm can be determined if the inhibitors effect is due mainly to the adsorption on the metal surface. The type of the adsorption isotherm can provide additional information about the properties of these tested compounds. The fractional surface coverage

ϴ can be easily determined from the weight loss measurements

$$\theta = \frac{W\circ - W}{W\circ} \qquad (5)$$

Where Wo and W are the corrosion rates without and with inhibitor.

The dependence of the fraction of the surface covered θ obtained by the ratio ƞ/100 as function of the concentration (C) of Hexaconazole and Bromuconazole was tested graphically by fitting it to various isotherms. Langmuir's isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. The surface coverage data for the studied compounds have failed to be linear when plotted C/θ versus C, suggesting that adsorption of Hexaconazole was according to Langmuir's isotherm:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

Were C is the concentration of the inhibitor, k is the adsorptive equilibrium constant, and θ is the surface coverage. And adsorption of Bromuconazole was not according to Langmuir's isotherm

Also, we have tested the different models:

Temkin isotherm

$$\exp(f.\theta) = K_{ads}.C \qquad (7)$$

Frumkin isotherm

$$\frac{\theta}{(1-\theta)}.exp\,(-2f.\theta) \quad = K_{ads}.C \qquad (8)$$

And Freundluich isotherm

$$\theta = K_{ads}.C \qquad (9)$$

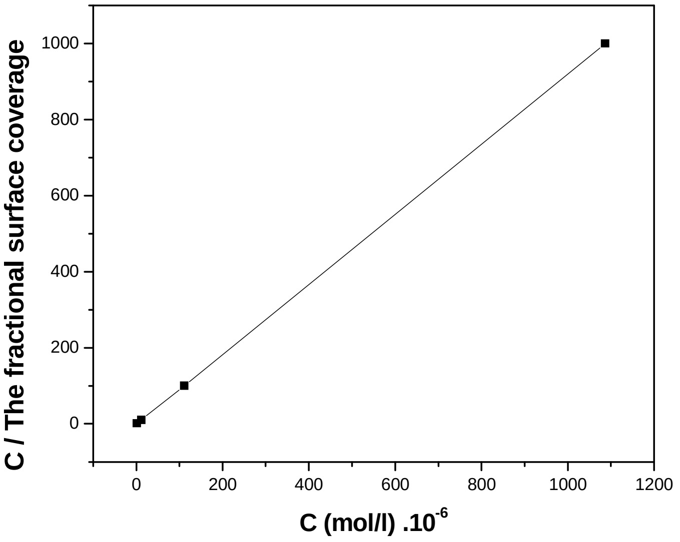

**Fig 11: Langmuir adsorption plots for ordinary steel in 1M HCL containing different concentrations of Hexaconazole**

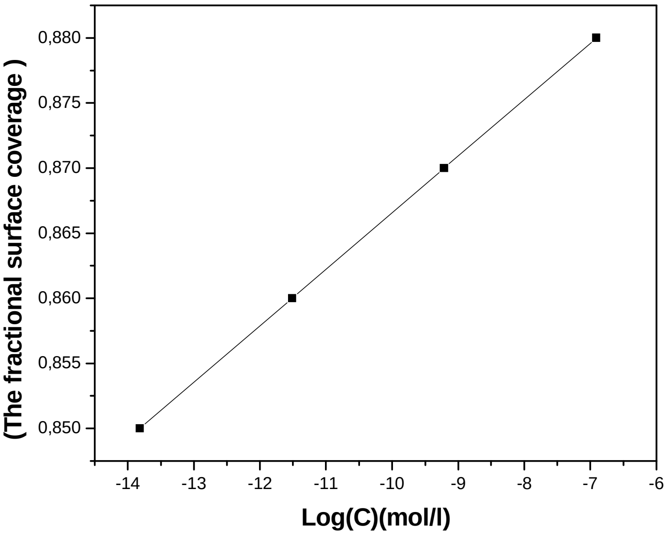

**Fig 12: Temkin's isotherm adsorption of Bromuconazole**

It seems from the various isotherm models tested that the alone straight line is obtained for Bromuconazole on plotting ϴ versus log C suggesting that the adsorption of the Bromuconazole on steel surface Follow Temkin's adsorption isotherm (Fig. 12) [23].

The free energy of adsorption was calculated according to the following equation

$$K = \frac{1}{55{,}5}\exp\left(-\frac{\Delta G°ads}{RT}\right) \qquad \boxed{(10)}$$

Where 55.5 is the molar concentration of water in the solution in mol l-1

These values were found to be -8Kj/mol, -24.45Kj/mol for Hexaconazole and Bromuconazole respectively, the negative values of ΔG°ads indicate spontaneous adsorption of the inhibitor on the metal surface [24-27].

The activation energy can be determined from Arrhenius plots for steel corrosion rate presented in by the following relation:

$$I = A\exp\left(-\frac{Ea}{RT}\right) \qquad \boxed{(11)}$$

Where T the absolute temperature, Ea the activation corrosion energy for the corrosion process and I is the corrosion current density.

The apparent activation energies (Ea) and pre-exponential factors (A) at are calculated by linear regression between ln(Icorr) and 1/T (Fig. 13) [23].

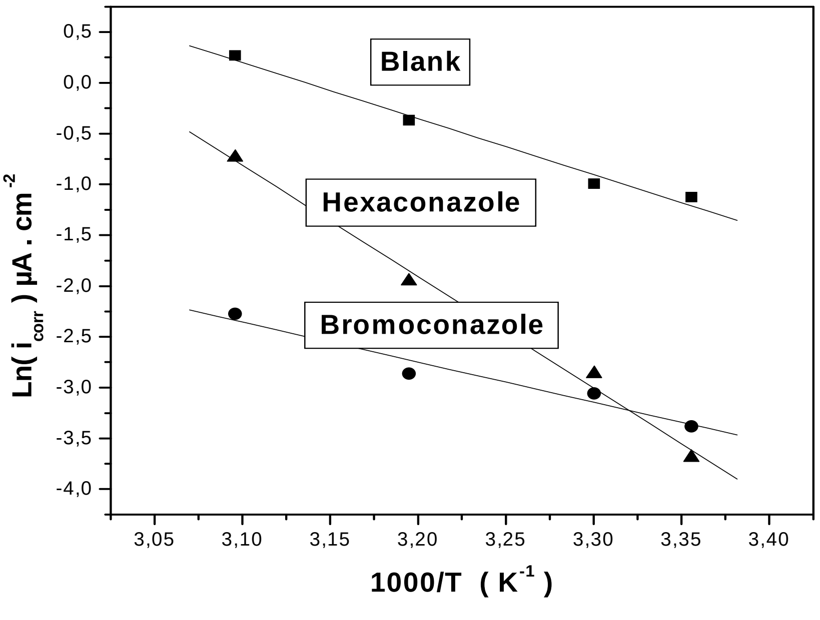

**Fig 13: Arrhenius slopes calculated from corrosion current density for mild steel in the absence and the presence of $10^{-3}$M of Bromuconazole and Hexaconazole**

**Table.5: The activation energies for the corrosion in the presence and absence of inhibitors**

| Inhibitor | A(µA.cm$^{-2}$) | Ea(Kj/mol) |
|---|---|---|
| Blank | $34{,}96.10^{6}$ | 45.92 |
| Hexaconazole | $25{,}95.10^{13}$ | 91.18 |
| Bromuconazole | $19{,}53.10^{3}$ | 28.45 |

The apparent activation corrosion energies in the absence and presence of the inhibitors were found to be 45.92 kj/mol Blank, 91.18 Kj /mol for Hexaconazole and 28.45 Kj /mol for Bromuconazole respectively. The pre-exponential factors (A) and Ea show the same trend. The increase in Ea in the presence of Hexaconazole may be interpreted as physical adsorption by the formation of an adsorptive film of an electrostatic character and Ea value in the presence of Bromuconazole with respect to the unhibited solution is typical of chimisorption on the steel surface [24].this result shown clearly that Bromuconazole has the best inhibiting efficiency at all temperature.

## CONCLUSION

The following main conclusions are drawn from the present study.

- Both isomers studied are excellent inhibitors for the corrosion of ordinary steel in 1 M HCl.
- The inhibition efficiency increases with inhibitor concentration to attain near 90% for both inhibitors at $10^{-3}$M.
- Inhibition of corrosion by Bromuconazole is due to the formation of a chemisorbed film on the metal surface and Hexaconazole is due to the formation of a physical adsorptive film.
- Adsorption of Bromuconazole on the surface of steel from 1M HCl obey Temkin's adsorption isotherm and adsorption of Bromuconazole on the surface of steel obey Langmuir's adsorption isotherm.
- The two inhibitor's act as mixed-type inhibitors.

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