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# Electrochemical behaviour of N,S-containing corrosion inhibitor for C38 Steel in molar HCl

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## ABSTRACT

*The influence of 2-phenylthieno (3,2-b) quinoxaline (P4) on the corrosion of steel in 1M HCl solution has been investigated by potentiodynamic polarisation and impedance spectroscopy (EIS) methods. The inhibiting action increases with the concentration of P4. The highest efficiency 95 % is obtained at the* $5x10^{-4}$ *M P4. We note good agreement between potentiodynamic polarisation and EIS methods. Polarisation measurements show also that P4 acts as a mixed inhibitor. The cathodic curves indicate that the reduction of proton at the steel surface happens with an activating mechanism.*

**Key words:** Quinoxaline, Inhibition, Corrosion, Steel, Acid.

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## INTRODUCTION

The studies of the inhibition of corrosion of mild steel are multiplied because of the wide use of this material in many operations such as pickling, cleaning, descaling, etc. Hydrochloric acid is often used because of the higher soluble ferrous chloride. To avoid damage and cost, inhibitors are added to secure metal dissolution and acid consumption [1–3]. The most effective and efficient inhibitors are organic compounds having π bonds and containing nitrogen, sulphur and oxygen in their structures. The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface which consists of the replacement of water molecule at a corroding interface as:

$$\mathbf{Org_{(sol)}+nH2O_{(ads)} \rightarrow Org_{(ads)}+nH2O_{(sol)}}$$

$Org_{(sol)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution that adsorbed to the metal surface.

The compounds containing both nitrogen and sulphur are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulphur [4-6]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. Among the efficient inhibitor, quinoxalines derivatives exhibited high efficiency in several acids and different metals [7-12]. The detailed study undertaken by gravimetric method of 2-phenylthieno (3, 2-b) quinoxaline (P4) at different concentrations and at various temperatures [13] have incited us to develop electrochemical (polarisation and EIS) measurements to insight more information about the inhibitory action of P4 on the corrosion of steel in 1 M HCl. It is the aim of the present work.

## MATERIALS AND METHODS

### 2. Experimental

The quinoxaline compound (P4) was synthesized from 3-methylquinoxalin-2-one as described in [13].

Electrochemical measurements were carried out in a conventional three electrode electrolysis cylindrical pyrex glass cell. The working electrode (W.E) had the form of a disc cut from the steel sheet. The area exposed to the corrosive solution was $1 cm^2$. A saturated calomel electrode (SCE) and a platinum electrode were used respectively as reference and auxiliary electrode. The temperature was thermostatically controlled at 308 °K. Running on an IBM compatible personal computer, the 352 Soft CorrTM III Software communicates with EG&G Instruments potentiostat-galvanostat model 263A at a scan rate of 20 mV/min.

Before recording the polarisation curves, the test solution was de-aerated and magnetically stirred for 30 min in the cell with nitrogen. The steel electrode, kept at its open circuit value, was polarised at -800 mV for 10 min. The potential of the electrode was then swept. Gas bubbling was maintained through the experiments. Electrochemical impedance spectroscopy (EIS) was carried out with a Tacussel electrochemical system which included a digital potentiostat model Voltalab PGZ 100 computer at $E_{corr}$ after immersion in solution without bubbling, the circular surface of steel exposing of $1 cm^2$ to the solution were used as working electrode. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation.

## RESULTS AND DISCUSSION

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

EIS is carried out by imposing potential sweeps, potential steps, or current steps, we typically drive the electrode to a condition far from equilibrium, and we observe the response, which is usually a transient signal. Another approach is to perturb the cell with an alternating signal of small magnitude and to observe the way in which the system follows the perturbation at steady state. Many advantages accrue to these techniques [14]. This measurement is equivalent to determining the faradic impedance. EIS is essentially a steady state technique that is capable of accessing relaxation phenomena whose relaxation times vary over orders of magnitudes and permits single averaging within a single experiment to obtain high precision levels. It confirms the conventional polarization techniques for corrosion rate measurements. The technique has been widely used in investigating corrosion inhibition processes [15]. It also provides information on both the resistive and capacitive behaviour at interface and makes possible to evaluate the performance of the tested compounds as possible inhibitors against metal corrosion [16].

Electrochemical impedance spectroscopy (EIS) measurements have been carried out at 308 K in acidic solution with and without quinoxaline compound (Fig 1.a). The charge-transfer resistance ($R_t$) values are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance ($C_{dl}$) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation:

$$C_{dl} = \left( \frac{1}{\omega . R_t} \right) \quad \text{where} \quad \omega = 2\pi f_{max}$$

The inhibition efficiency got from the charge transfer resistance is calculated by:

$$E_Z (\%) = 100 \,.\, ( 1 - R_t / R_{t/inh} )$$

$R_t$ and $R_{t/inh}$ are the charge transfer-resistance values without and with inhibitor, respectively.

The impedance diagram obtained with 1 M HCl shows only one depressed capacitive loop at the higher frequency range. The same trend was also noticed for C38 steel immersed in 1 M HCl containing P4 (5 $10^{-6}$M–5 $10^{-4}$ M). In Table 1, impedance parameters of the Nyquist plots of the P4 in different concentrations are given. $R_t$ is a measure of electron transfer across the surface and is inversely proportional to corrosion rate.

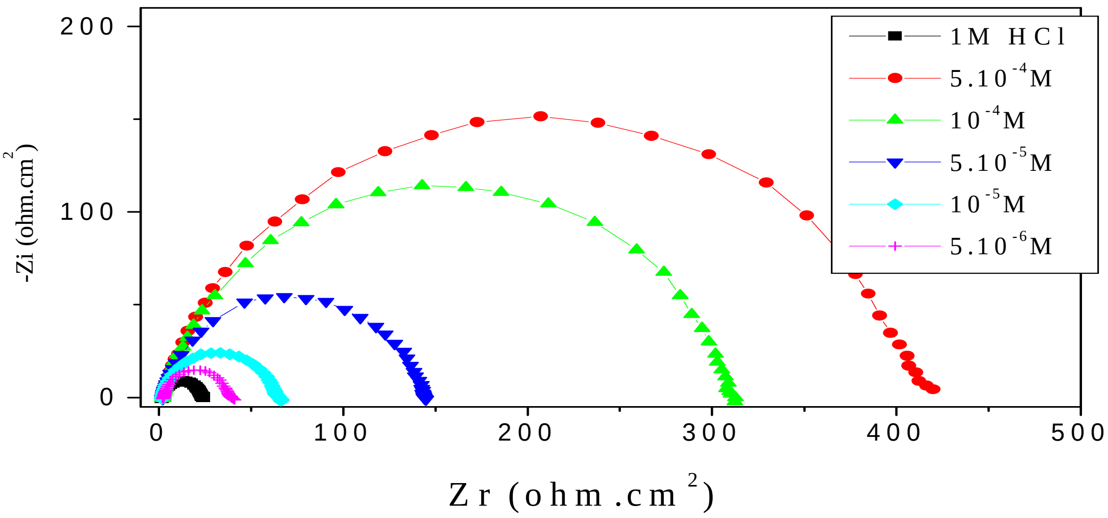

**Fig. 1a. Nyquist plots of steel in 1M HCl containing various concentrations of P4 at $E_{corr}$.**

The most common equivalent circuit used to model corrosion of C-steel in aqueous acidic solution is the Randles circuit. The HF capacitive loop could be attributed to the double layer capacity in parallel with the charge-transfer resistance ($R_t$) (Fig. 1.c) [17]. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [18]. The diameter of Nyquist plots increases on increasing the P4 concentration. This suggested that the formed inhibitive film was strengthened by addition of P4. Besides, the presence of low frequency (LF) inductive may be attributed to the relaxation process obtained by adsorption species like $Cl_{ads}^{-1}$ and $H_{ads}^{+}$ on the electrode surface. It should be noted that a CPE could be treated as a parallel combination of a pure capacitor and a resistor being inversely proportional to the angular frequency. The CPE, which is considered a surface irregularity of the electrode, causes a greater depression in Nyquist semicircle diagram, where the metal–solution interface acts as a capacitor with irregular surface [19].

Electrical equivalent circuits are generally used to model the electrochemical behaviour and to compute the parameters of interest. When there is non-ideal frequency response, it is common practice to use distributed circuits elements in the equivalent circuit (Fig. 1.c). The most widely used is the constant phase element (CPE) which has a non-integer power dependence on the frequency.

**Table.1. Impedance parameters for Steel in 1M HCl for various concentrations of P4.**

| | Concentration (M) | $R_p$ ($\Omega.cm^2$) | $R_s$ ($\Omega.cm^2$) | $R_t$ ($\Omega.cm^2$) | $f_{max}$ (Hz) | $C_{dl}$ ($\mu F/cm^2$) | E (%) |
|---|---|---|---|---|---|---|---|
| Blank | 1 | 23.78 | 1.38 | 22.4 | 79.33 | 89.6 | - |
| P4 | $5x10^{-6}$ | 39.35 | 1.90 | 37.3 | 53.03 | 80.5 | 39.9 |
| | $10^{-5}$ | 66.53 | 1.63 | 64.9 | 31.69 | 77.4 | 65.5 |
| | $5x10^{-5}$ | 148.68 | 1.78 | 146.9 | 15.91 | 68.1 | 84.7 |
| | $10^{-4}$ | 326.11 | 1.81 | 324.3 | 7.81 | 62.8 | 93.1 |
| | $5x10^{-4}$ | 436.26 | 1.76 | 434.5 | 6.08 | 60.2 | 94.8 |

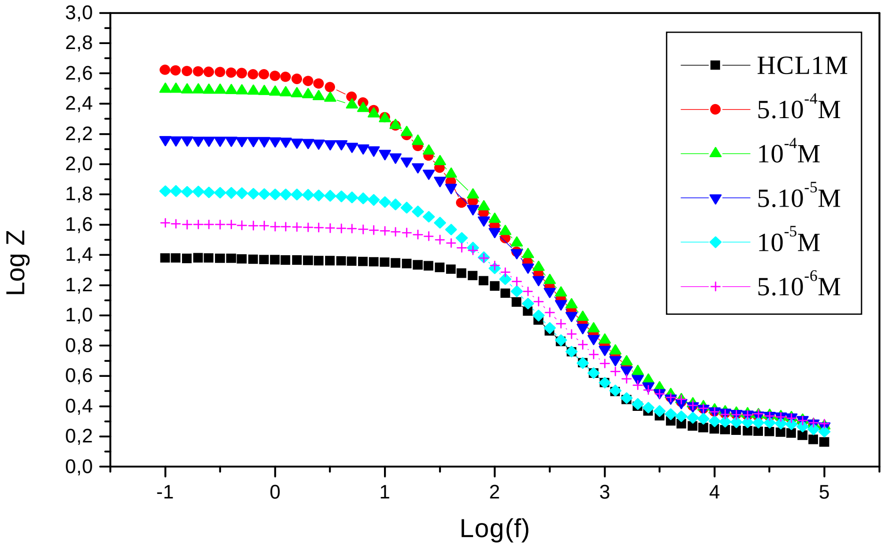

**Fig. 1.b Bode diagrams for steel in 1M HCl containing different concentrations of P4.**

In most times, CPE is required for modelling the frequency dispersion behaviour corresponding to different physical phenomena such as surface heterogeneity which results from surface roughness, impurities, dislocations, distribution of the active sites, adsorption of inhibitors and formation of porous layers [20,21].

As it can be seen from Table 1, the $R_t$ values increased with the increasing the concentrations of the inhibitors. On the other hand, the values of $C_{dl}$ decreased with an increase in the inhibitors concentration thus with inhibition efficiencies. This situation was the result of an increase the surface coverage by the inhibitor, which led to an increase in the inhibition efficiency. This decrease in the $C_{dl}$ can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, signifying that quinoxaline molecule acts by adsorption at the solution/interface [22].

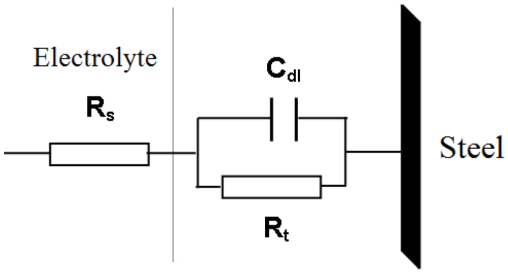

**Fig. 1.c Electrochemical equivalent circuit diagram for metal–electrolyte interface.**

The impedance spectra obtained on iron in 1 M HCl solutions consist of one depressed capacitive loop (one time constant in the Bode-phase representation (Fig. 1.b). When Nyquist plot contains a ‘‘depressed semicircle with the center under the real axis, such behavior is characteristic for solid electrodes and often referred to as frequency dispersion has been attributed to roughness and other inhomogeneities of the solid surface [23-25]. In these cases the parallel network charge transfer resistance double layer capacitance ($R_t/C_{dl}$) is usually a poor approximation especially for systems where an efficient inhibitor is present. For the description of a frequency independent phase shift between an applied AC potential and its current response.

*3.2. Polarisation results.*

The influence of concentration of P4 on the cathodic polarisation curves of steel in 1M HCl is studied at 308 K. Fig. 2 shows the typical curves obtained by P4 addition. Table.2 gives values of corrosion current ($I_{corr}$) obtained by extrapolation of the Tafel lines, corrosion potential ($E_{corr}$), cathodic Tafel slope ($\beta_c$). In this case, the relation determines the inhibition efficiency ($E_I$%):

$$E_I\%=\left(1-\frac{I_{corr}}{I^{o}_{corr}}\right).100$$

$I°_{corr}$ and $I_{corr}$ are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

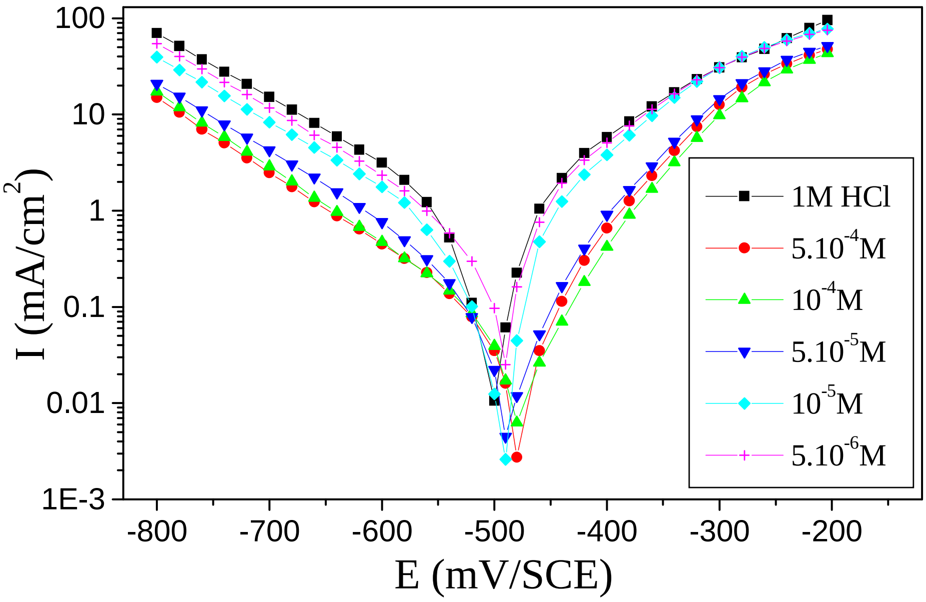

**Fig. 2. Polarisation curves of steel in 1M HCl for various concentrations of P4**

The data in Table 2 indicate that the $I_{corr}$ values gradually decreased with the increase of the inhibitor concentration with respect to the blank. From this decrease it could be concluded that the rate of anodic dissolution and that of the cathodic hydrogen evolution are much retarded. Also, some decrease in the corresponding values of the cathodic Tafel slopes were observed, too. This means that P4 must have acted predominantly by blocking both anodic and cathodic sites to some extent behaving as a mixed type acid corrosion inhibitor.

**Table.2 Electrochemical parameters of steel in 1M HCl and P4 at various concentrations and the corresponding inhibition efficiency**

| | Concentration (M) | $E_{corr}$ (mV/SCE) | $\beta_c$ (mV/dec) | $I_{corr}$ ($\mu A/cm^2$) | E (%) |
|---|---|---|---|---|---|
| Blank | 1 | -502 | 147.9 | 912 | - |
| P4 | $5x10^{-6}$ | -486 | 145.1 | 545.8 | 40.1 |
| | $10^{-5}$ | -493 | 143.1 | 347.7 | 61.8 |
| | $5x10^{-5}$ | -491 | 137.7 | 173.8 | 80.9 |
| | $10^{-4}$ | -479 | 127.9 | 79.1 | 91.3 |
| | $5x10^{-4}$ | -481 | 132.1 | 61.1 | 93.3 |

From this decrease it could be concluded that the rate of anodic dissolution and that of the cathodic hydrogen evolution are much retarded. Also, some decrease in the corresponding values of the cathodic Tafel slopes were observed, too. This means that P4 must have acted predominantly by blocking anodic sites and also cathodic sites to some extent behaving as a mixed type acid corrosion inhibitor.

## CONCLUSION

The following conclusions are made:

- 2-phenylthieno (3, 2-b) quinoxaline (P4) is an efficient inhibitor for steel in 1 M HCl.
- The inhibition efficiency of P4 attains a maximum value of about 95 % at $510^{-4}$ M.
- P4 act as a mixed type inhibitor with modifying the mechanism of hydrogen evolution.

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