SOME TETRAZOLIC COMPOUNDS AS CORROSION INHIBITORS
FOR COPPER IN NITRIC ACID MEDIUM

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The corrosion inhibition of copper in 0.1 M HNO₃ was studied by gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements by the use of tetrazolic compounds such as 1,2,3,4-tetrazole (TTZ), 1-phenyl-1,2,3,4-tetrazole (PT), 5-amino-1,2,3,4-tetrazole (AT) and 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT). The addition of these compounds acts differently on the kinetic of corrosion process of copper in nitric medium. The comparative study indicates that PMT is the best inhibitor. Its inhibition efficiency increases while its concentration increases in solution to attain 97 % at 10⁻³ M. Electrochemical measurements show that both polarization and transfer resistances increase with PMT concentration. The adsorption of PMT on the copper surface followed the Frumkin isotherm model. The results obtained from the various methods are in good agreement.

Keywords: thermodynamic analysis in alternative energy, corrosion, inhibition, copper, nitric acid, tetrazole



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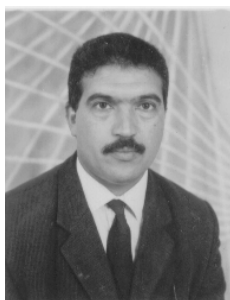
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Publications: More than 16 papers in corrosion and pesticide.

Introduction

Numerous investigations have been performed on the corrosion inhibition of copper and its alloys by the use of different organic compounds [1-9]. Among the practical interest of these later are the chemical bond that linked

the inhibitors and the metal. Therefore, the organic inhibitors provide often an excellent protection against corrosion phenomenon. This protection was explained by the presence of heteroatoms (S, N, P, Se) in the molecular structure of the inhibitors [8-12].

The addition of an inhibitor at certain concentration minimises the direct interaction between the metal and corrosive agents. In some cases, the coordination of the inhibitor molecules to the surface is weak, and their presence in the corrosive solutions required maintaining the desired concentration of these agents to attain a minimal protection of the metal [10-13]. As some inhibitor molecules also serve as reducing agents for the copper oxidation products, they must be continuously added to avoid other possible type of corrosion [14].

In the last few decades, numerous investigations were performed by using the traditional electrochemical methods [15-17], but recently, many research groups try to understand processes taking place at electrode surfaces by using in situ different accelerated corrosion techniques coupled by surface sensitive techniques like quartz crystal microbalance (QCM) and scanning probe microscopy (SPM) [18-22]. These in situ techniques have fostered a better understanding of dissolution/deposition of metals and adsorption of different ions by measuring mass differences in order of nanogram per surface area or visualizing the surface morphological changes in nanometer or even atomic scale. Related to this issue, several investigations [23-27] reported that the inhibition effectiveness might be due to the formation of thin layers of copper-inhibitor complexes. It's found also that 5-mercapto-1-phenyl-tetrazole (PMT) was an efficient inhibitor against the dissolution of various metals in different acid mediums [5, 6, 28]. This molecule adsorbs probably through the sulphur atom or through coordination with nitrogen from the tetrazole ring [29]. Ye et al. [30] demonstrate also that copper surface is normally coated with cuprous oxide layer (Cu_2O), and PMT forms protective barriers of inert, insoluble and long-lasting polymeric Cu(I) complex coating on the Cu_2O substrate.

The aim of this paper is to study the corrosion behaviour of copper in 0.1 M HNO_3 in the presence and in the absence of the tetrazolic compounds at 25 °C by the use of gravimetric measurements combined with linear potential scan voltammetry (I-E) and electrochemical impedance spectroscopy (EIS) methods.

Experimental methods

Materials

The material used was prepared from copper (99.99 %). The specimens used in the gravimetric tests have a rectangular form (2×3 cm). For the electrochemical studies, the electrode was provided in rod form and was embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a copper wire threaded into the base of the metal sample. The surface of the specimen was 0.35 cm^2 . Prior to each test, the exposed surfaces were abraded successively with different emery paper up 1200 grade, washed thoroughly with acetone and rinsed with double distilled water. The experiments were carried out in aerated 0.1M HNO_3 solution which was prepared using analytical grade

reagent (65 %) and double distilled water. All experiments have been performed at temperature 25 ± 1 °C. Tetrazolic compounds tested (at 10^{-3}M) were 1,2,3,4-tetrazole (TTZ), 1-phenyl-1,2,3,4-tetrazole (PT), 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT), and 5-amino-1,2,3,4-tetrazole (AT). They are Aldrich commercial products (> 99 % purity). Their molecular structures are shown in Fig. 1.

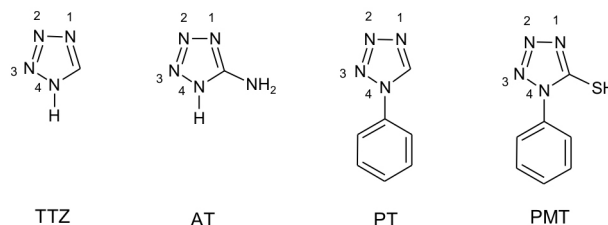


Fig. 1. Molecular structures of organic compounds tested

Gravimetric and electrochemical measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. All experiments were carried out under total immersion in 75 ml of test solutions at temperature 25 °C. Mass loss was recorded by an analytical balance with 0.1 mg accuracy at 72 hours of immersion.

Steady-state polarization experiments were conducted with a potentiostat PGP 201. The polarization curves were obtained by means of the linear potential sweep of 60 mV min^{-1} after the working electrode was left under free corrosion (for about 30 min) to reach a stable potential. The electrochemical measurements were performed in a conventional three-electrode electrochemical cell (Tacussel Standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrodes, respectively.

Electrochemical impedance spectroscopy (EIS) was carried out with a voltalab PGZ 100 electrochemical system at E_{corr} after immersion in solution. After determination of the steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz was superimposed on the rest potential. Computer programs (Voltmaster4) automatically controls the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams were given in the Nyquist representation.

Results and discussion

Comparative study

The effect of the addition of tetrazolic compounds on the corrosion of copper in aerated nitric acid solution was studied by gravimetric measurements after 72 hours of immersion period and at 25 °C. The concentration of these inhibitors of 10^{-3}M was chosen to compare the inhibition efficiency of the four compounds toward the

generalised corrosion. The value of the inhibition efficiency ($E_G/\%$) was determined using the equation (1).

$$E_G = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100, \quad (1)$$

where W_{corr} and W'_{corr} ($\text{mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$) are the corrosion rate in absence and presence of the inhibitor, respectively.

The corrosion data for different inhibitors tested are reported in Table 1.

Table 1

Corrosion rate of copper in 0.1 M HNO_3 with and without tetrazole at 10^{-3} M, and the corresponding inhibition efficiency

| Solution | $W_{corr} / \mu\text{g cm}^{-2}\cdot\text{h}^{-1}$ | $E_G / \%$ |
|----------|--|------------|
| Blank | 3.65 | - |
| TTZ | 2.50 | 31 |
| AT | 1.51 | 58 |
| PT | 0.20 | 94 |
| PMT | 0.09 | 97 |

According to this data, it is clear that the addition of tetrazolic compounds reduces the corrosion rate of copper in nitric acid solution. The inhibition efficiency was found to depend on the nature of substituents.

Potentiokinetic polarization curves were plotted for copper in 0.1M HNO_3 solution in the presence of TTZ, PMT, AT or PT at 10^{-3} M (Fig. 2).

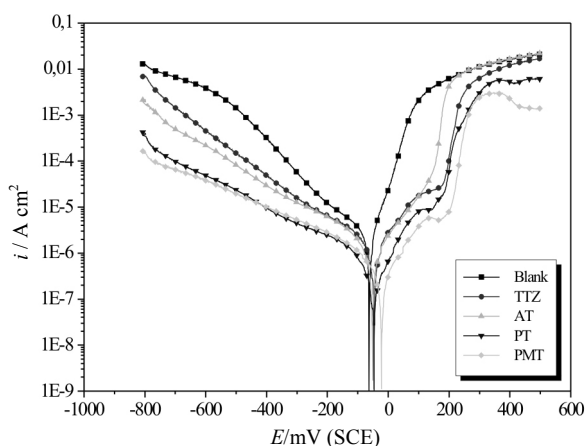


Fig. 2. Polarization curves of copper in 0.1 M HNO_3 with and without tetrazole at 10^{-3} M

A linear region with apparent Tafel was observed. The cathodic reaction was activation-controlled and the addition of the compounds tested decreased the current densities in large anodic and cathodic domains of potential. This result indicated that the compounds studied acted as mixed-type inhibitors. Generally, the

addition of mixed inhibitors in solution does not change corrosion potential significantly because they inhibit both the anodic and cathodic reactions. Small changes in potentials can be a result of the competition of the anodic and the cathodic inhibiting reactions, and of the metal surface condition.

Table 2 gives the values of the associated electrochemical parameters.

Table 2

Electrochemical parameters of copper in 0.1 M HNO_3 with and without tetrazole at 10^{-3} M, and the corresponding inhibition efficiencies

| Solution | $E_{corr} / \text{mV (SCE)}$ | $I_{corr} / \mu\text{A cm}^{-2}$ | $R_p / \Omega \text{cm}^2$ | $\beta_c / \text{mV dec}^{-1}$ | $E_I / \%$ | $E_{Rp} / \%$ |
|----------|------------------------------|----------------------------------|----------------------------|--------------------------------|------------|---------------|
| Blank | -63 | 4.3 | 4050 | -85 | - | - |
| TTZ | -49 | 3.0 | 5525 | -73 | 30 | 27 |
| AT | -54 | 1.7 | 11065 | -74 | 60 | 63 |
| PT | -51 | 0.3 | 92500 | -75 | 94 | 96 |
| PMT | -27 | 0.2 | 133320 | -75 | 95 | 97 |

The inhibition efficiency ($E_I / \%$) was determined using the equation (2) :

$$E_I = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100, \quad (2)$$

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

From Table 2, it was clearly seen that cathodic slope was found equal indicating that the reduction of hydrogen did not modified in the presence of the inhibitors tested. Thus, the presence of tetrazolic compounds at 10^{-3} M leads to decrease in the values of I_{corr} , which was particularly significant in the case of PMT.

The inhibition properties of tetrazolic compounds were evaluated also by polarization resistance method. Fig. 3 presents plots of the current densities as a function of over-voltage near the corrosion potential E_{corr} .

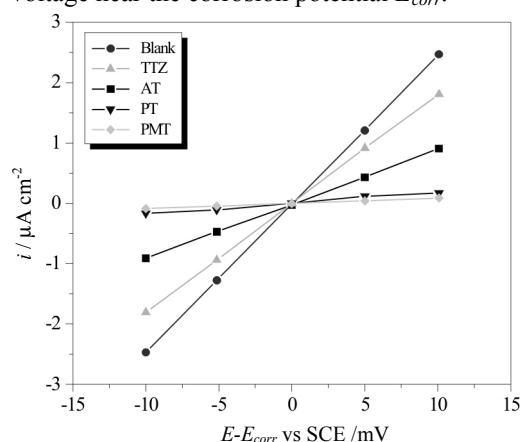


Fig. 3. Linear polarization curves of copper in 0.1 M HNO_3 with and without tetrazole at 10^{-3} M

Table 2 gathered the corresponding values of polarization resistance R_p and the inhibition efficiency (E_{Rt} / %) which is calculated using the equation (3).

$$E_{Rt} = \frac{R_p' - R_p}{R_p'} \times 100, \quad (3)$$

R_p and R_p' are the polarization resistance values without and with inhibitor, respectively.

From polarization resistance measurements, the weakest value of R_p is found for copper in 0.1 M HNO_3 without inhibitor. However, the addition of the tetrazole in solution leads to an increase in the polarization resistance values. In fact, the value of R_p is $5525 \Omega \text{ cm}^2$ in the case of TTZ and increases for AT ($11065 \Omega \text{ cm}^2$), PT ($92500 \Omega \text{ cm}^2$) and PMT ($R_p = 133320 \Omega \text{ cm}^2$). This in turn leads to a decrease in corrosion current density I_{corr} values because this later is inversely proportional to R_p .

Furthermore, corrosion behaviour of copper, in acidic solution with and without addition of tetrazole at 10^{-3} M, is investigated by electrochemical impedance spectroscopy (EIS) measurement at corrosion potential (E_{corr}) and after 30 min of immersion (at 25°C). The corresponding Nyquist diagrams are shown in Fig. 4.

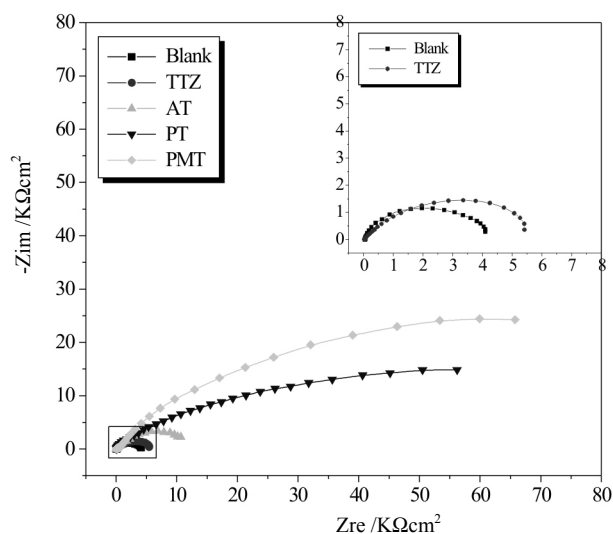


Fig. 4. Nyquist plots obtained for copper in 0.1 M HNO_3 without and with tetrazole at 10^{-3} M (at E_{corr})

The charge-transfer resistance (R_t) values are calculated from the difference in impedance at low and high frequencies, as suggested by Tsuru et al. [31]. The double layer capacitance (C_{dl}) was obtained, at the frequency f_m at which the imaginary component of the impedance is maximum ($-Z_{im}$), using the equation (4):

$$C_{dl} = \frac{1}{2\pi f_m R_t}. \quad (4)$$

The impedance parameters derived from this investigation are mentioned in Table 3.

Table 3
Impedance parameters for copper in 0.1 M HNO_3 with and without addition of tetrazolic inhibitors at 10^{-3} M, and the corresponding inhibition efficiency

| Solution | $R_s / \Omega \text{ cm}^2$ | $R_t / \Omega \text{ cm}^2$ | f_m / Hz | $C_{dl} / \mu\text{F cm}^{-2}$ | $E_{Rt} / \%$ |
|----------|-----------------------------|-----------------------------|-------------------|--------------------------------|---------------|
| Blank | 14 | 4096 | 0.63 | 61.6 | - |
| TTZ | 16 | 6020 | 0.63 | 41.9 | 32 |
| AT | 18 | 13250 | 0.4 | 30.0 | 69 |
| PT | 21 | 90770 | 0.2 | 8.7 | 95 |
| PMT | 22 | 135170 | 0.2 | 5.9 | 97 |

The inhibition efficiency (E_{Rt} / %) got from the charge-transfer resistance is calculated using the following equation:

$$E_{Rt} = \frac{R_t' - R_t}{R_t'} \times 100 \quad (5)$$

R_t and R_t' are the charge-transfer resistance values without and with inhibitors, respectively.

As we notice, Fig. 4, the impedance diagram, corresponds to the blank, shows perfect semi-circle indicating a charge transfer process mainly controlling the corrosion of copper. The addition of tetrazolic compounds enhances the value of the transfer resistance in acidic solution. EIS study confirms that the tested compounds are efficient inhibitors.

From the impedance data reported in Table 3, the values of R_t increase according to the sequence $\text{TTZ} < \text{AT} < \text{PT} < \text{PMT}$. This behaviour reveals the adsorption of inhibitors on the copper surface, and an increasing in the values of corrosion inhibition efficiency. The value of double-layer capacitance decreases in the presence of tetrazole. This decrease confirms the adsorption of these compounds on the metal surface leading to a film formation on the copper surface. The inhibition efficiency obtained from EIS measurement are close to those deduced from polarization and gravimetric methods.

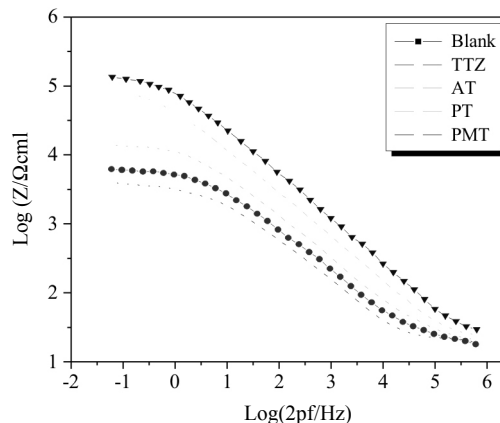


Fig. 5. Bode plots of copper in 0.1 M HNO_3 containing different tetrazolic compounds at 10^{-3} M (at E_{corr})

As the impedance diagrams obtained in the case of PT and PMT inhibitors, the semi-circles are more nonperfect. In this subject, several studies showed that the semi-circle is imperfect while the inhibition effect of the inhibitors is important [32-36].

Fig. 5 shows the Bode plots on the electrodes made of these samples.

The EIS results for the liquid and steam-treated samples can be explained by the simple equivalent Randles circuit [37], Fig. 6, which consist of a solution resistance R_s in series with a component composed of parallel film capacitance C_{dl} and transfer resistance R_t [38].

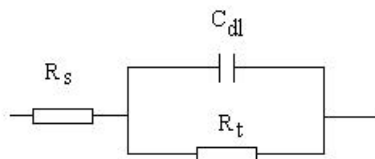


Fig. 6. A simple Randles-type equivalent circuit for EIS measurements

The values of the inhibition efficiency obtained from different methods are in good agreement. Therefore, the inhibiting effect was found to increase according to the following sequence: TTZ < AT < PT < PMT.

This order is mainly due to the nature of the substituents and its position. It's well known that different substituents on the organic molecule polarize the functional group in a different manner [39] and the inhibition efficiency of organic inhibitor containing heteroatoms should follow the sequence $O < N < S < P$ [40]. The presence of NH_2 in AT, phenyl in PT, SH and phenyl in PMT may increase the polarity and the adsorbability of inhibitors on the metal surface. Therefore, the inhibition efficiency of TTZ is about 30 % and increases to 63 % in the cases of AT, then it attains 97 % with PMT. These jumps may be explained by the calculation of the net atomic charges [41]. The net charge of sulphur atom being -0.061 e, is adsorbed on the surface of metal. The presence of both phenyl and SH groups in PMT leads to synergistic intramolecular effect (Table 4) [30, 42-43].

Table 4

Net atomic charges of tetrazolic compounds calculated by PETRA program [41]

| Inhibitor | N(1) | N(2) | N(3) | N(4) | S | E_{LUMO} / eV | E_{HOMO} / eV | ΔE / eV |
|-----------|---------|---------|---------|--------|--------|-----------------|-----------------|-----------------|
| TTZ | -0.2439 | -0.1391 | -0.1743 | 0.1502 | - | -0.085 | -11.413 | 11.32 |
| AT | -0.1658 | -0.1101 | -0.1176 | 0.1950 | - | 0.018 | -10.084 | 10.10 |
| PT | -0.2212 | -0.1165 | -0.1559 | 0.1852 | - | -0.765 | -9.893 | 9.128 |
| PMT | -0.2258 | -0.1132 | -0.1701 | 0.1826 | -0.061 | -0.800 | -9.418 | 8.618 |

The calculation shows that $N(4)$ with positive charge does not participate to the adsorption phenomenon. Yan et al. [44] revealed that 2-mercaptobenzoxazole (MBO) is the good inhibitor toward copper corrosion in NaCl solution. Their studies show that the inhibition film (MBO-Cu) causes shift of N_{1s} and S_{2p} binding energies. Consequently, it could be inferred that the presence of mercapto group and nitrogen atom in the molecule could have an important role in the formation of the inhibition film.

The computation of some of quantum chemical parameters such as the energies of the molecular orbitals, E_{HOMO} (High Occupied Molecular Orbital Energy) and E_{LUMO} (Lowest Unoccupied Molecular Orbital Energy), has been determined for possible relations with the inhibitor efficiencies of the inhibitors tested (Table 4). HOMO energy is often associated with the electron donating ability of a molecule. The less negative HOMO energy and the smaller energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) are often interpreted by a stronger chemisorption bond and perhaps greater inhibition efficiency [45, 46]. The plot of the inhibition efficiency of tetrazolic compounds against E_{HOMO} showed a linear correlation of slope equal to unity and regression coefficient $R = 0.99$ (Fig. 7). The similar results were obtained elsewhere [47].

From the results of the comparative study, it's evident that PT and PMT were the excellent corrosion inhibitors

for copper in nitric acid medium. Afterwards of this work, we proposed doing a detailed study of PMT in order to better understand its inhibition mechanism.

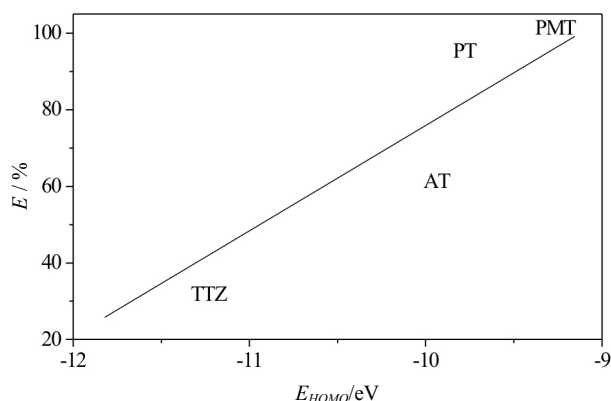


Fig. 7. Correlation of HOMO energies with percent inhibition efficiency of tetrazole derivatives

Effect of PMT concentration

Table 5 regroups the gravimetric parameters (W_{corr} and E_G / %) of copper in 0.1M HNO_3 in the presence of PMT at different concentrations after 72 h of period immersion.

Table 5
Corrosion rate of copper in 0.1 M HNO₃ with PMT at different concentration, and the corresponding inhibition efficiencies at $T = 25^\circ\text{C}$

| [PMT] | $W_{\text{corr}} / \mu\text{g cm}^{-2}\cdot\text{h}^{-1}$ | $E_G / \%$ |
|-------------|---|------------|
| Blank | 3.65 | - |
| 10^{-9} M | 1.83 | 50 |
| 10^{-8} M | 1.45 | 60 |
| 10^{-7} M | 0.65 | 82 |
| 10^{-6} M | 0.50 | 86 |
| 10^{-5} M | 0.38 | 90 |
| 10^{-4} M | 0.20 | 94 |
| 10^{-3} M | 0.09 | 97 |

According to this data, it's clear that the corrosion rate of copper in the blank is higher in comparison with the blank containing PMT. The addition of 10^{-9} M PMT into the aggressive medium reduces this corrosion rate by 51 % and reaches 97 % at 10^{-3} M. The inhibition efficiency of PMT increases as function of its concentration and exceeds 90 % from 10^{-5} M. Fig. 8 presents the evolution of the current densities as function of the over-voltage near of the corrosion potential E_{corr} .

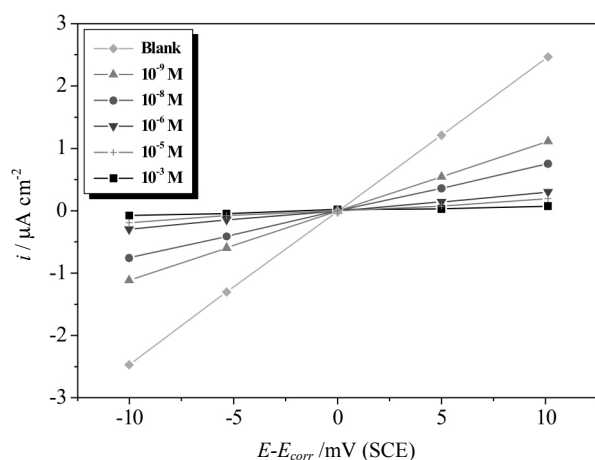


Fig. 8. Linear polarization curves of copper in 0.1 M HNO₃ with PMT at different concentration

The corrosion parameters such as the values of polarization resistance R_p and corresponding inhibition efficiencies ($E_{R_p} / \%$) are shown in Table 6.

From the polarization resistance measurement (Fig. 8, Table 6), the polarization resistance R_p related to the copper in 0.1 M HNO₃ is the lower value. However, R_p was found to increase with the rise of PMT concentration. This result was accompanied with an increase of the inhibition efficiencies.

The effect of the addition of PMT at different concentration on the corrosion behaviour of copper in

0.1 M HNO₃ was studied also by the use of electrochemical impedance spectroscopy (EIS) measurements. The impedance diagrams and the corresponding electrochemical parameters are shown, respectively, in Fig. 9 and Table 6.

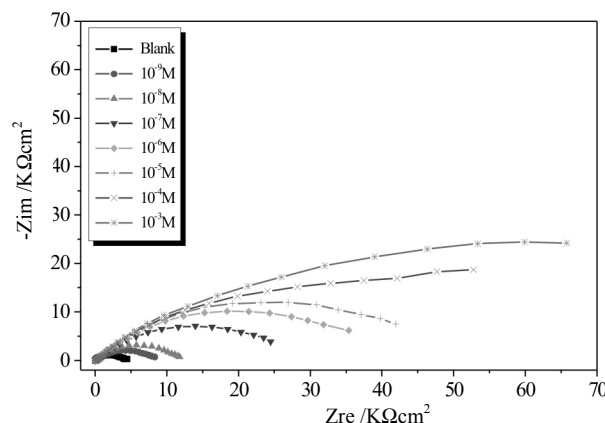


Fig. 9. Nyquist plots obtained for copper in 0.1 M HNO₃ with PMT at different concentrations

Table 6
Polarization resistance and impedance parameters of copper in 0.1 M HNO₃ in the presence of PMT at various concentrations, and the corresponding inhibition efficiencies

| [PMT] | $R_p / \Omega \text{ cm}^2$ | $R_t / \Omega \text{ cm}^2$ | f_m / Hz | $C_d / \mu\text{F cm}^{-2}$ | $E_{R_p} / \%$ | $E_{R_t} / \%$ |
|-------------|-----------------------------|-----------------------------|-------------------|-----------------------------|----------------|----------------|
| Blank | 4050 | 4096 | 0.63 | 61.7 | - | - |
| 10^{-9} M | 9010 | 8340 | 0.63 | 30.3 | 55 | 51 |
| 10^{-8} M | 13135 | 12250 | 0.63 | 20.6 | 69 | 66 |
| 10^{-7} M | 20250 | 26180 | 0.40 | 15.2 | 80 | 84 |
| 10^{-6} M | 34033 | 37990 | 0.35 | 12 | 88 | 89 |
| 10^{-5} M | 52600 | 50070 | 0.3 | 10.6 | 92 | 92 |
| 10^{-4} M | 67500 | 90450 | 0.2 | 8.8 | 94 | 95 |
| 10^{-3} M | 132320 | 135170 | 0.2 | 5.9 | 97 | 97 |

The impedance diagrams obtained have, generally, a semicircular appearance. It indicates that the corrosion of copper is mainly controlled by a charge transfer process. The interaction of the tested molecule with the metal surface should be competitive with the interaction of the ions in the solution. In this case, the chemisorption has occurred. The adsorption would have occurred through polar centres as nitrogen and sulphur atoms. As for the shape of the impedance diagrams obtained, more nonperfect semi-circulars were found above 10^{-5} M concentration. This explains that PMT is very efficient at high concentrations. The similar results were found elsewhere [32-36].

From the impedance data, we conclude that increasing of PMT concentration provokes an increase of the value of

R_i and consequently the inhibition efficiency values. This behaviour shows the adsorption of PMT on copper surface which is approved also by the decrease of the values of double-layer capacitance as function of the concentration of PMT. This decrease may be due to the film formation on the copper surface [28, 30, 48-50].

Data were tested graphically by fitting to various isotherms. Fig. 10 shows the dependence of the fraction (θ) as function of the logarithm of the concentration of PMT, where θ is the ratio ($E/\%$)/100.

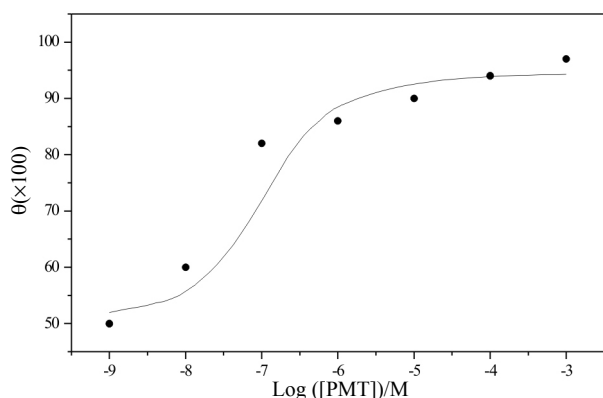


Fig. 10. Frumkin isotherm adsorption of PMT on the copper surface in 0.1M HNO₃

The obtained plot is consistent with an S-shape adsorbed isotherm for PMT showing an adsorption on the copper surface according to the Fumkin isotherm.

$$\frac{\theta}{1-\theta} \exp(-f\theta) = KC \quad (6)$$

with

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^{\circ}}{RT}\right), \quad (7)$$

where ΔG_{ads}° is the free enthalpy of adsorption and f is a function of adsorption energy. The average value of k , f and ΔG_{ads}° calculated from $\theta = \text{Log} ([\text{PMT}])$ curve are:

$$f = -8.52; K = 13.5 \cdot 10^9 \text{ and } \Delta \Delta G_{ads}^{\circ} = -67.7 \text{ kJ} \cdot \text{mol}^{-1}.$$

The negative value of ΔG_{ads}° indicates that strongly adsorbed on the copper surface. Literature shows that more negative than -40 kJ mol^{-1} indicating chemisorption of PMT molecules. Moreover, the inhibition of copper by PMT is often explained by formation of Cu(II)-PMT through its heteroatoms [30].

Conclusion

The inhibiting effect of tetrazolic compounds in 0.1 M HNO₃ on copper was studied by various methods. The results are in good agreement and the main conclusions are as follows.

- The corrosion inhibition efficiency ($E/\%$) of tetrazolic compounds follows the sequence: TTZ < AT < PT < PMT.
- PMT was found to be the best inhibitor for copper.
- The inhibition efficiency of PMT exceeds 90 % above concentration of 10^{-5} M .
- PMT adsorbs on the copper surface according to the Frumkin adsorption isotherm. The value of ΔG_{ads}° indicates that PMT adsorbs strongly and spontaneously.

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