

CORROSION INHIBITION OF CARBON STEEL BY USING SOME BENZOTRIAZOLE DERIVATIVES IN 0.5M H₂SO₄ MEDIUM

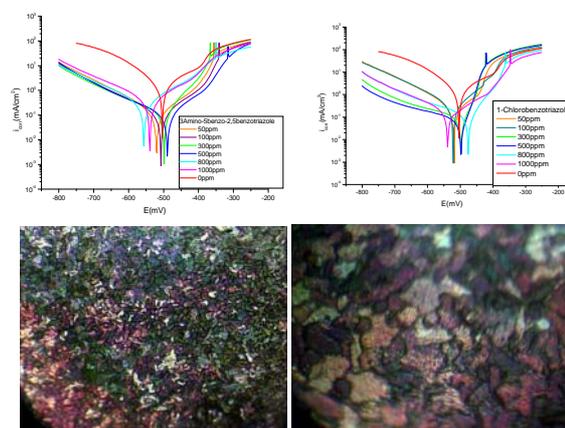
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The inhibitory effect of some benzotriazole derivatives 5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 mercato-1,2,4 benzotriazole on the corrosion behavior of carbon steel in 0.5M H₂SO₄ medium at temperature of 25°C was studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR) and metallurgical microscopy techniques. The effect of inhibitor concentration on the corrosion rate, surface coverage and inhibition efficiency is investigated. Results show that these organic inhibitors exert a strong inhibiting effect on carbon steel corrosion and acts as a mix-type inhibitor. The inhibition efficiency of organic inhibitors may be due to either the adsorption of inhibitor molecules building a protective film or the formation of an insoluble complex of the inhibitor adsorption obeys the Langmuir model. Further, characterization using FT-IR demonstrates the adsorption of inhibitors and the formation of corrosion products on the carbon steel surface. EIS results confirm its corrosion inhibition ability.



INTRODUCTION

Carbon steel is widely used in many applications; this intensified the research in corrosion resistance in various aggressive environments.¹⁻⁴ Acid solutions are large scale used in many industrial processes. Acid sulphuric, acid phosphoric and hydrochloric acid are aggressive solutions used for acid pickling of steel and ferrous alloys, acid cleaning and acid rescaling due to their special chemical properties. Treatment of the corrosive medium for the protection of metals can be realized through elimination of the corrosive species or through the use of inhibitors. The use of inhibitors is one of the most important

methods for protection of carbon steel against corrosion in acidic media.⁵⁻⁸ Through all inhibitors, the most important are the organic ones, also called adsorption inhibitors. As they usually affect the whole metal surface, when are present in sufficient concentration, they cannot be called anodic or cathodic inhibitors. Many organic compounds containing polar groups including nitrogen, sulphur and oxygen and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit corrosion for carbon steel in various aggressive environments.⁹⁻¹³ The inhibiting action of these organic compounds is usually attributed to their interactions with the metal surface by adsorption. The effect of some

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triazole derivatives has been reported earlier as corrosion inhibitors for steel, and they reveal that the inhibition efficiencies of these compounds are much greater than that of the corresponding amines and aldehydes. There are few reports about the successful use of Schiff base derived from aromatic aldehydes and amines, compounds containing aminic nitrogen as corrosion inhibitors for carbon steel in acidic media.¹⁴⁻¹⁹ Recently, the application of triazole derived Schiff bases as corrosion inhibitors has been studied by some authors, suggesting that Schiff bases have good inhibition properties for the corrosion of many metals in various aggressive media. The available data show that these compounds were selected as inhibitors. In the present work, the aim of this study is to report on the inhibition effect of some benzotriazole derivatives: 5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 benzo-2,5 benzotriazole on the corrosion behavior of carbon steel in 0.5M H₂SO₄ medium at temperature of 25°C. In this study, the inhibition of carbon steel corrosion in 0.5M H₂SO₄ by organic compounds was investigated by potentiodynamic polarizations, electrochemical impedance spectroscopy (EIS), Fourier transforms infrared spectroscopy (FT-IR) measurements and metallography analysis.

EXPERIMENTAL

All benzotriazole derivatives (5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 mercato-1,2,4 benzotriazole) were of analytical grade acquired from Fluka. Bidistilled water was used for solution preparations. The studied metals were the carbon steels type OL 37 with composition: C% 0.15; Si% 0.09; Mn% 0.4; Fe% 99.293; P% 0.023; S% 0.02; Al% 0.022; Ni% 0.001; Cr% 0.001. The working electrode for electrochemistry measurements was prepared from a cylindrical carbon steel rod with area 0.5 cm². This shape is preferred, because it ensures a greater surface and a reduce number of edges. The working electrode was mechanically polished on wet silicon carbide (SiC) papers (1200, 2500, 4000 grid) rinsed with bidistilled water, degreased with acetone and ethanol and dried at room temperature. The aggressive environment used was 0.5M H₂SO₄ solution prepared from analytical reagent grade chemicals and bidistilled water.

The polarization behavior of carbon steel in aqueous solutions of 0.5M H₂SO₄ in presence and absence of organic inhibitors has been studied by potentiostatic and potentiodynamic methods. The inhibitory action was studied through tracing the polarization curves obtained using the potentiodynamic method calculation of the kinetic parameters of corrosion in case of solutions with inhibitors, especially the corrosion current densities, and their comparison with the kinetic parameters of the solution without inhibitors. The

polarization curves were obtained by potentiostatic and potentiodynamic methods.

Potentiostatic, potentiodynamic and EIS measurements were carried out by using the conventional three electrodes set up; the cell was connected to an automated model VoltaLab 40 potentiostat/galvanostat. A platinum sheet served as counter electrode (CE), a saturated calomel electrode (SCE) as the reference electrode and a working electrode made of carbon steel type OL37. All the potential values gives in this study were measurements with respect to this electrode at a temperature of 25°C. Fourier transform infrared spectroscopy (FT-IR) was used to identify whether there was adsorption of organic inhibitor on the surface of the metal was performed with Bruker Optics. Metallurgical microscopy techniques was obtained with Hund H600 microscope.

RESULTS AND DISCUSSION

In this study, the inhibition of the corrosion is the result of the adsorption of the organic compound on the metal surface forming an invisible film of a few molecular diameters thickness. The inhibition activity analysis of the organic compound was made by assuming that the mechanism of inhibition by organic molecules is chemisorption

The polarization behaviour of carbon steels mentioned above was studied through the plotting of the polarization curves obtained using the potentiodynamic method, finding the kinetic parameters of corrosion (especially the density of the corrosion current) from solutions without inhibitors and their comparison with the kinetic parameters from solutions with different concentrations of inhibitor. The corresponding Tafel parameters were obtained by Mansfeld's method, employing polarization data near the corrosion potential. In the present paper, when values of $E-E_{cor}$ are higher than about 70 mV, slight but significant changes in the anodic and cathodic Tafel slopes were found. Figs. 1-3 show a series of potentiodynamic polarization curves of carbon steels electrode in (it was not aerated) in absence and presence of different concentrations of benzotriazole derivatives.

Both anodic and cathodic polarization curves for carbon steel in 0.5M H₂SO₄ at various concentrations of this benzotriazole derivatives are shown in Figs. 1-3. It is clear that the presence inhibitors cause a markedly decrease in the corrosion rate, i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This can be assigned to adsorption of inhibitor over the carbon steel surface.

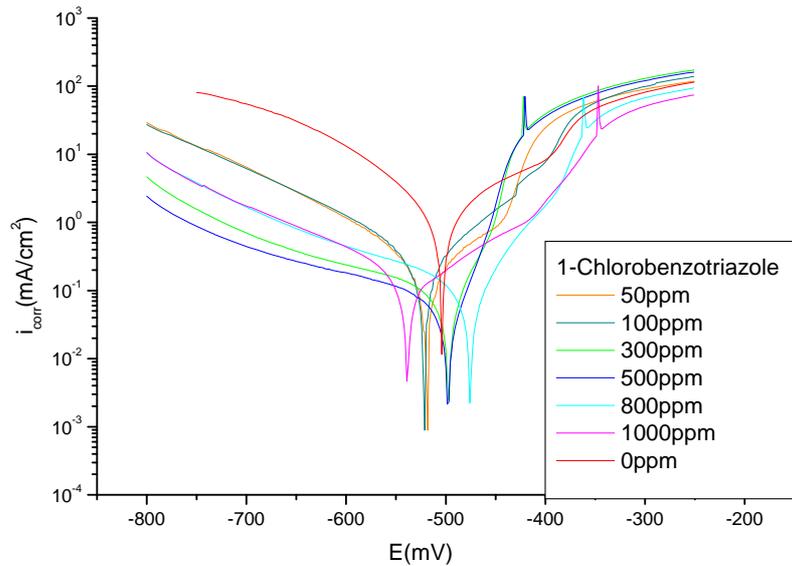


Fig. 1 – Polarization curves of OL 37 in 0.5M H₂SO₄+Xppm 5-Chlorobenzotriazole at temperature of 25°C.

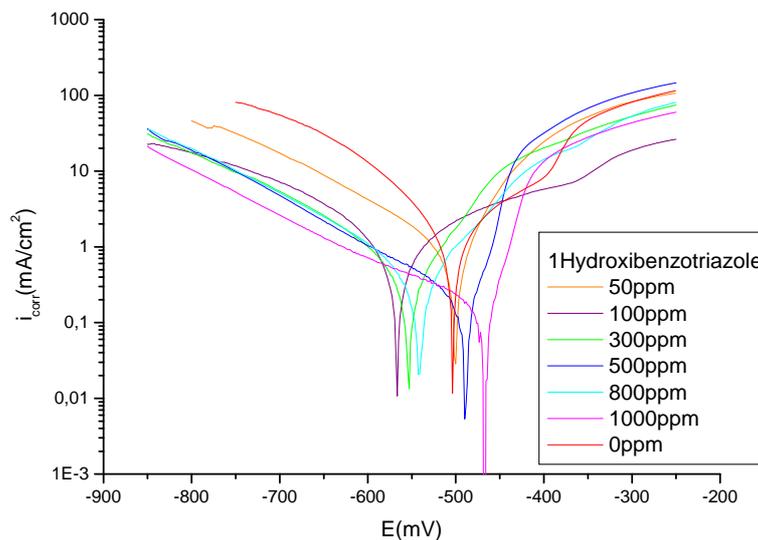


Fig. 2 – Polarization curves of OL 37 in 0.5M H₂SO₄+Xppm 1-Hydroxybenzotriazole at temperature of 25°C.

The results suggest that the three inhibitors act as a mixed-type inhibitor with predominant cathodic effectiveness for chlorobenzotriazole, which works mainly by increasing the hydrogen evolution potential in the H₂SO₄ solution, makes the corrosion potential negative shift and slows the cathodic and anodic process of the carbon steel. Thus, the corrosion reaction of OL 37 is inhibited.

Analysis of the polarization curves from Figs. 1-3 indicates that the maximum efficiency is obtained at the inhibitor concentration of 300ppm and 500ppm for the system: 5-Chlorobenzotriazole+OL37-H₂SO₄, 500 ppm and 1000ppm for the system: 1-Hydroxybenzotriazole+OL37-H₂SO₄, 100ppm and 500ppm for the system 3-amino-5 mercato-1,2,4 benzotriazole +OL37-H₂SO₄. At the increasing inhibitor concentration over these concentrations (300 ppm and 500 ppm) the inhibitor efficiency starts

to decrease, respectively the corrosion current densities begin to increase again.

Electrochemical corrosion kinetics parameters, *i.e.* corrosion current density (i_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a , b_c), R_p (polarization resistance) obtained from the Tafel extrapolation of the polarization curves were given in Tables 1-3. Analyzing these tables, it can be observed that the addition of the organic inhibitor to the amounts shown in Tables 1-3 leads in all the cases to inhibition of the corrosion process. All the studied of these organic inhibitors (5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 mercato-1,2,4 benzotriazole) showed a very good inhibition properties for the corrosion of carbon steel in 0.5M H₂SO₄ and the corrosion current density decreased and the inhibitor efficiency increased with increasing inhibitors concentrations.

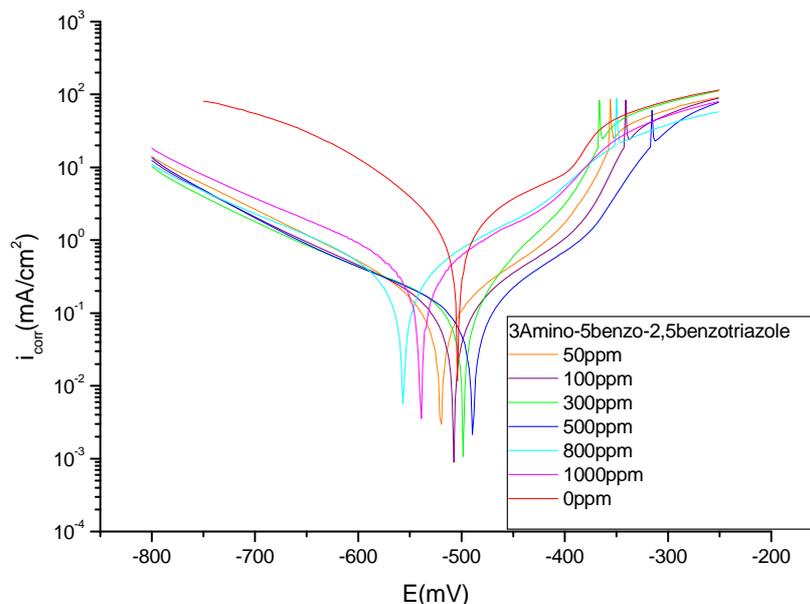


Fig. 3 – Polarization curves of OL 37 in 0.5M H_2SO_4 +Xppm 3-amino-5 mercato-1,2,4 benzotriazole at temperature of 25°C.

Table 1

Kinetic corrosion parameters of OL 37 in 0.5M H_2SO_4 in presence and absence of organic inhibitor type 5-chlorobenzotriazole at temperature of 25°C

| Concentration (ppm) | i_{corr} (mAcm ⁻²) | R_p Ωcm ⁻² | R_{mpy} | $P_{mm/year}$ | K_g g/m ² h | E (%) | $-E_{corr}$ (mV) | b_a (mVdec ⁻¹) | $-b_c$ (mVdec ⁻¹) | θ |
|---------------------|----------------------------------|-------------------------|-----------|---------------|--------------------------|-------|------------------|------------------------------|-------------------------------|----------|
| 0 | 1.095 | 14.16 | 511 | 12.96 | 11.61 | - | 506 | 101 | 83 | |
| 50 | 0.146 | 90.23 | 68.13 | 1.729 | 1.543 | 86.6 | 520 | 83 | 79 | 0.86 |
| 100 | 0.205 | 71.94 | 95.66 | 2.428 | 2.17 | 81.25 | 522 | 81 | 91 | 0.81 |
| 300 | 0.0415 | 201.7 | 19.36 | 0.491 | 0.44 | 96.22 | 500 | 35 | 72 | 0.96 |
| 500 | 0.0158 | 277 | 7.37 | 0.187 | 0.167 | 98.55 | 498 | 24 | 35 | 0.98 |
| 800 | 0.0993 | 171.7 | 46.34 | 1.176 | 1.053 | 90.93 | 478 | 61 | 169 | 0.90 |
| 1000 | 0.073 | 133 | 34.06 | 0.864 | 0.774 | 93.33 | 539 | 91 | 59 | 0.93 |

Table 2

Kinetic corrosion parameters of OL 37 in 0.5M H_2SO_4 in presence and absence of organic inhibitor type 1Hydroxybenzotriazole at temperature of 25°C

| Concentration (ppm) | i_{corr} (mAcm ⁻²) | R_p Ωcm ⁻² | R_{mpy} | $P_{mm/year}$ | K_g g/m ² h | E (%) | $-E_{corr}$ (mV) | b_a (mVdec ⁻¹) | $-b_c$ (mVdec ⁻¹) | θ |
|---------------------|----------------------------------|-------------------------|-----------|---------------|--------------------------|-------|------------------|------------------------------|-------------------------------|----------|
| 0 | 1.095 | 14.16 | 511 | 12.96 | 11.61 | - | 506 | 101 | 83 | |
| 50 | 0.692 | 20.65 | 323.16 | 8.202 | 7.34 | 36.75 | 503 | 54 | 113 | 0.36 |
| 100 | 0.452 | 28.9 | 211 | 5.35 | 4.79 | 58.7 | 568 | 86.6 | 76 | 0.59 |
| 300 | 0.291 | 45.52 | 135.8 | 3.44 | 3.086 | 73.34 | 556 | 68 | 86 | 0.73 |
| 500 | 0.204 | 72.37 | 95.3 | 2.42 | 2.16 | 81.33 | 491 | 31 | 145 | 0.81 |
| 800 | 0.333 | 52.28 | 155 | 3.944 | 3.52 | 70 | 544 | 85 | 112.5 | 0.70 |
| 1000 | 0.172 | 88 | 80.59 | 2.045 | 1.83 | 84.22 | 472 | 23 | 435 | 0.84 |

Table 3

Kinetic corrosion parameters of OL 37 in 0.5M H_2SO_4 in presence and absence of organic inhibitor type 3-amino-5 mercato-1,2,4 benzotriazole at temperature of 25°C

| Concentration (ppm) | i_{corr} (mAcm ⁻²) | R_p Ωcm ⁻² | R_{mpy} | $P_{mm/year}$ | K_g g/m ² h | E (%) | $-E_{corr}$ (mV) | b_a (mVdec ⁻¹) | $-b_c$ (mVdec ⁻¹) | θ |
|---------------------|----------------------------------|-------------------------|-----------|---------------|--------------------------|-------|------------------|------------------------------|-------------------------------|----------|
| 0 | 1.095 | 14.16 | 511 | 12.96 | 11.61 | - | 506 | 101 | 83 | - |
| 50 | 0.088 | 188 | 41.1 | 1.04 | 0.934 | 91.9 | 521.6 | 96 | 98 | 0.91 |
| 100 | 0.085 | 209 | 39.66 | 1.01 | 0.90 | 92.23 | 508 | 93 | 118 | 0.92 |
| 300 | 0.096 | 163 | 45.12 | 1.145 | 1.025 | 91 | 502 | 62 | 141 | 0.91 |
| 500 | 0.087 | 213 | 40.6 | 1.03 | 0.923 | 92 | 490 | 90.3 | 144 | 0.92 |
| 800 | 0.226 | 83 | 105 | 2.676 | 2.39 | 89 | 557 | 107 | 123 | 0.89 |
| 1000 | 0.266 | 69 | 124 | 3.15 | 2.82 | 76 | 540 | 105 | 113 | 0.75 |

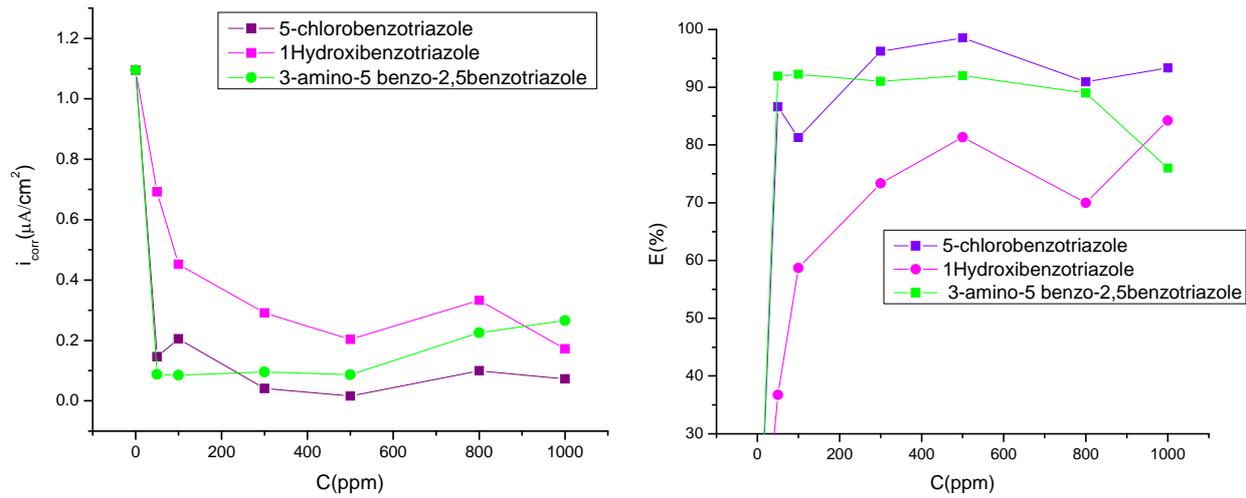


Fig. 4 – The influence of the inhibitors 5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 benzo-2, 5 benzotriazole concentration on the corrosion rate and efficiency of the carbon steel in 0.5M H_2SO_4 at 25°C.

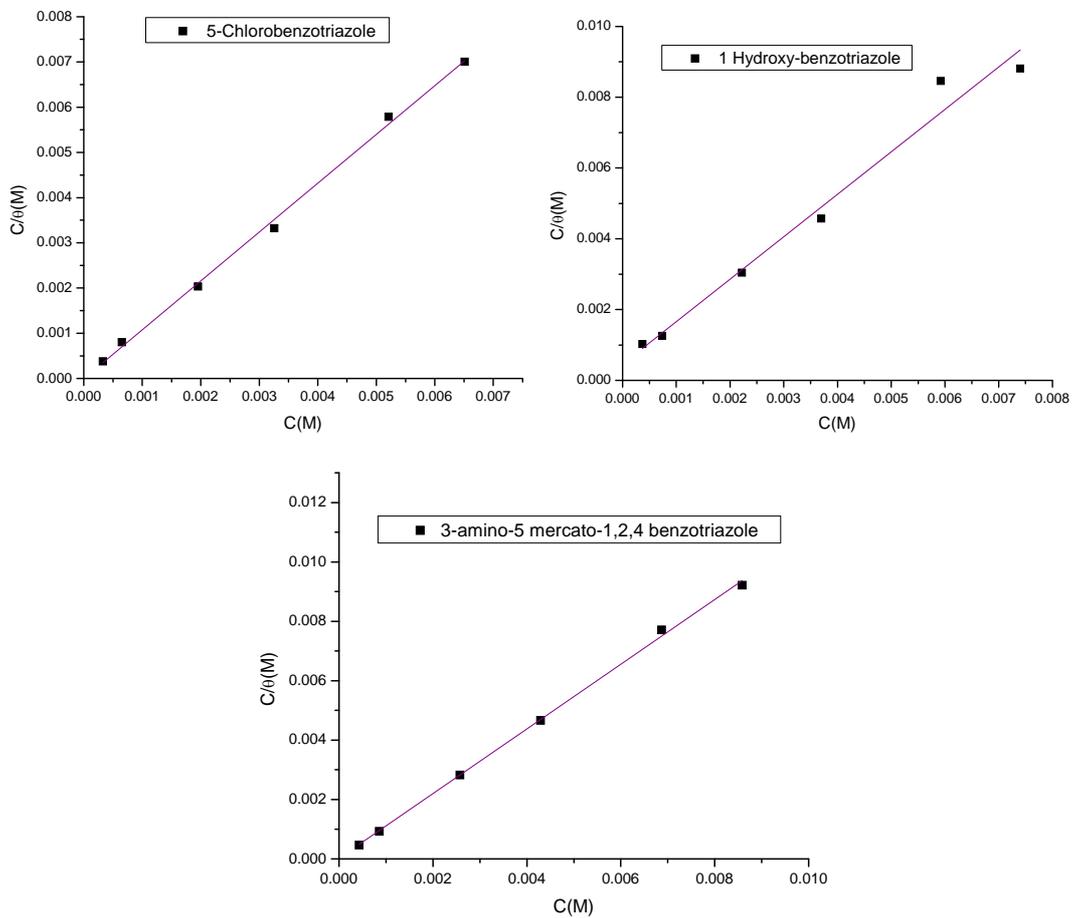


Fig. 5 – Langmuir plot for 5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 mercato-1,2,4 benzotriazole in 0.5M H_2SO_4 at different inhibitor concentrations.

The variation of inhibition efficiency and current density with inhibitor concentrations is shown in Fig. 4. The inhibition efficiency increased with increase in concentration and from Fig. 4, one can see much better the influence of

these parameters on the polarization behaviour of the carbon steel in 0.5M H_2SO_4 (see Fig. 4). It is obvious from the figures that all these compounds inhibit the corrosion of carbon steel

in 0.5M H₂SO₄ at all concentrations used in this study.

Adsorption of organic compounds can be described by two main types of interaction: physical adsorption and chemisorption processes, which are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. To quantify the effect of inhibitor concentration on the corrosion rate, it is common to fit the rate data to equilibrium adsorption expressions, such as Langmuir equation: $\theta/(1-\theta)=KC$, where θ is the fraction of surface coverage by the inhibitor and K is the equilibrium constant for the adsorption reaction. θ is given by: $\theta = (i_{\text{corr}} - i_{\text{inh}})/i_{\text{corr}}$, where i_{inh} and i_{corr} are the corrosion rates in 0.5M H₂SO₄ with and without inhibitor. Usage of the Langmuir treatment is often justified with the argument that inhibition must involve adsorption.

In this study, the Langmuir isotherm is plotted against C , when a linear relationship is obtained for each inhibitor and a slope of near unity for each compound indicated approximate Langmuir behavior (see Fig. 5). Moreover, we shall try to show what kind type of adsorption process takes place on the electrode surface. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on brass surface.

The adsorption equilibrium constant (K_{ads}) is related to the standard free energy of reaction ($\Delta G_{\text{ads}}^{\circ}$) by the equation: $\ln K_{\text{ads}} = -(\Delta G_{\text{ads}}^{\circ} / RT)$.

The negative values of $\Delta G_{\text{ads}}^{\circ}$ suggest that the adsorption of inhibitor molecule onto carbon steel surface is a spontaneous process. The values of up to -20kJmol^{-1} are consistent with electrostatic interaction between the charged molecules and the charged metal – physical adsorption, while those more negative than -40kJmol^{-1} imply sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinative type of

bond – chemisorption. It can be seen from table 4 that the value of $\Delta G_{\text{ads}}^{\circ}$ is around -33.73KJM^{-1} for 5Chlorobenzotriazole and -27.0173KJM^{-1} for 3Amino-5benzo-2,5 benzotriazole, which indicate the adsorption of this inhibitors is mainly the chemisorption, the value of $\Delta G_{\text{ads}}^{\circ}$ is around -19.05KJM^{-1} for 1-Hydroxy-benzotriazole which indicate the adsorption of this inhibitor is the physical adsorption.

The impedance response of OL 37 in 0.5M H₂SO₄ solution showed significant changes after addition of the inhibitors. This indicates that the impedance of carbon steel increases with increasing the inhibitor concentration.

The Nyquist diagram obtained with 0.5M H₂SO₄ shows only one capacitive loop and the diameter of the semicircles increases on increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitors.

The obtained impedance spectra do not present perfect semicircle, which can be seen as depressed capacitive loops. This phenomenon is characteristic for solid electrodes and often corresponds to frequency dispersion which has been attributed to roughness and other in homogeneities of electrode surface. The semicircular appearance shows that the corrosion of steel is controlled by charge transfer and the presence of inhibitor does not change the mechanism of dissolution. Fig. 6 also indicates that the diameters of the capacitance loops in the presence of 500ppm and 300ppm 5-Chlorobenzotriazole +OL37 in 0.5MH₂SO₄, 300ppm and 500ppm 3-amino-5 mercato-1,2,4 benzotriazole +OL37-0.5MH₂SO₄ and for 1000ppm 1-Hydroxy-benzotriazole +OL37-0.5MH₂SO₄ are bigger than those in the absence of organic inhibitors, suggesting that has good anticorrosion performance on the carbon steel in 0.5M H₂SO₄.

Table 4

The values of K_{ads} and $\Delta G_{\text{ads}}^{\circ}$ for studied systems

| The system | Type of metallic material | Values of K_{ads} , M^{-1} | Values of $\Delta G_{\text{ads}}^{\circ}$ KJM^{-1} | Type of adsorption |
|--|---------------------------|--|---|---------------------------------------|
| 5Chlorobenzotriazole+0.5M H ₂ SO ₄ | OL-37 | $8.25 \cdot 10^5$ | -33.73 | Chemisorption and Physical adsorption |
| 1-Hydroxy-benzotriazole+0.5M H ₂ SO ₄ | OL-37 | $2.92 \cdot 10^3$ | -19.05 | Physical adsorption and Chemisorption |
| 3-amino-5 mercato-1,2,4 benzotriazole +0.5M H ₂ SO ₄ | OL-37 | $5.461 \cdot 10^4$ | -27.01 | Chemisorption and Physical adsorption |

Bode diagrams presented in Fig. 7 are in accordance with Nyquist diagrams. It can be observed that in absence of organic inhibitor the electrode presents one time constant corresponding to a phase angle of about 40° at medium and low frequencies, this fact indicates an inductive behaviour with low diffusive tendency. On the contrary, in the presence of the organic inhibitor, on the curve-phase angle versus log frequency appears a maximum very well defined corresponding to a phase angle of about $75-80^\circ$ which means that in this case the electrode has a strong capacitive behaviour, according with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams. Bode diagrams shows that the values of the impedance and phase angle also increase gradually with increasing inhibitor concentration, indicating the formation of a protective film.

The equivalent circuit that describes our metal/electrolyte interface is shown in Fig. 8,

where for analysis of the impedance spectra containing a single capacitive semicircle, the standard Randle's circuit is used (Fig. 8), as the circuit is composed of R_s , refer to solution resistance, R_{ct} charge transfer resistance and CPE constant phase element, respectively.¹⁹⁻²⁴ The high frequency limits correspond to R_s , while the lower frequency limits corresponds to R_s+R_{ct} . The resistor R_s capacitance is series to R_{ct} and R_{ct} is parallel in to the double layer capacitance.

Polarization curves and EIS results consistently indicate that this organic inhibitor protects the surface from corrosion. This is indicated by the increases in charge transfer resistance and the decrease in double layer capacitance, which are in turn the consequence of the participation of the benzotriazole derivatives inhibitor in the protective layer.

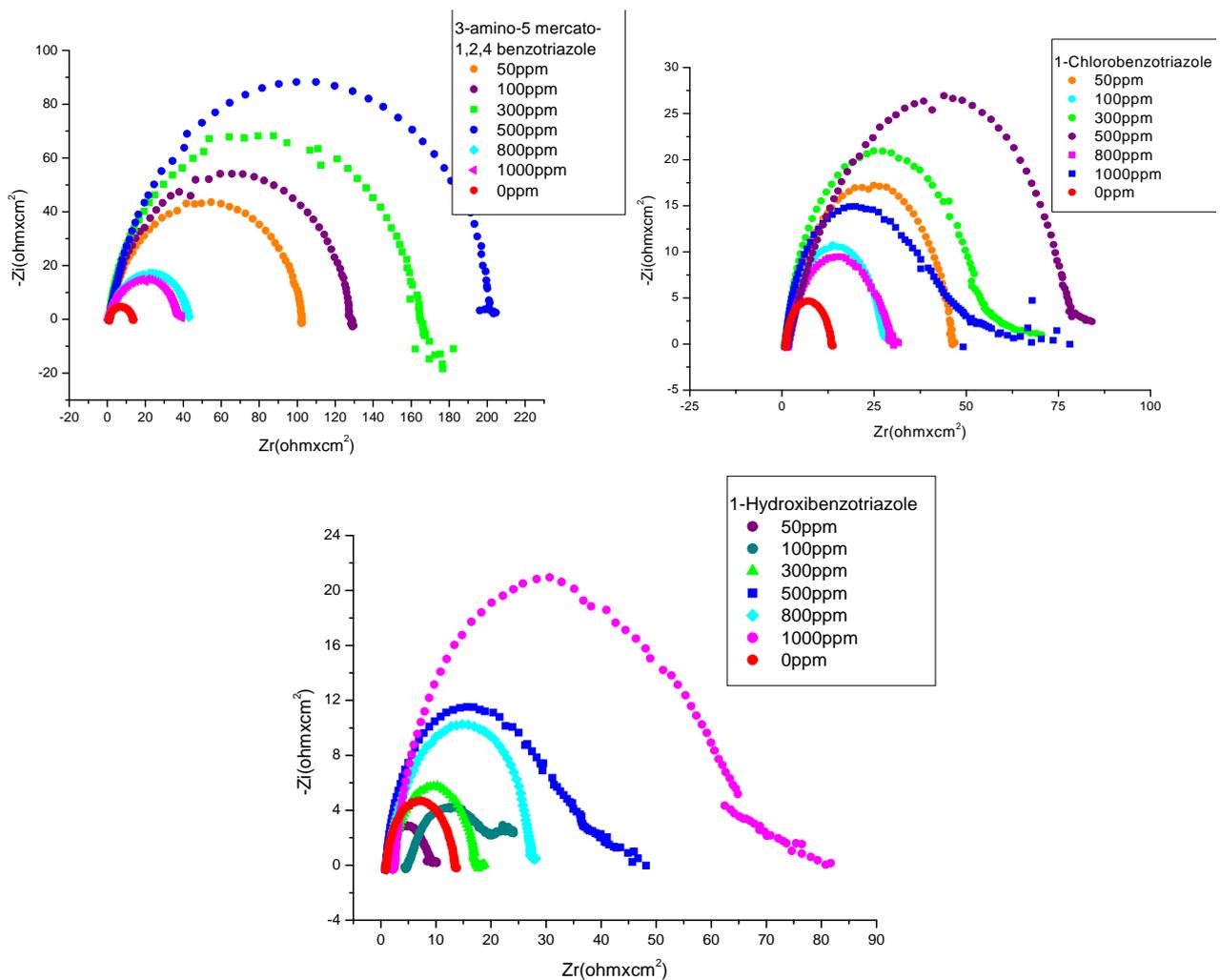


Fig. 6 – The Nyquist plot for OL37 in 0.5M H_2SO_4 with and without organic inhibitor.

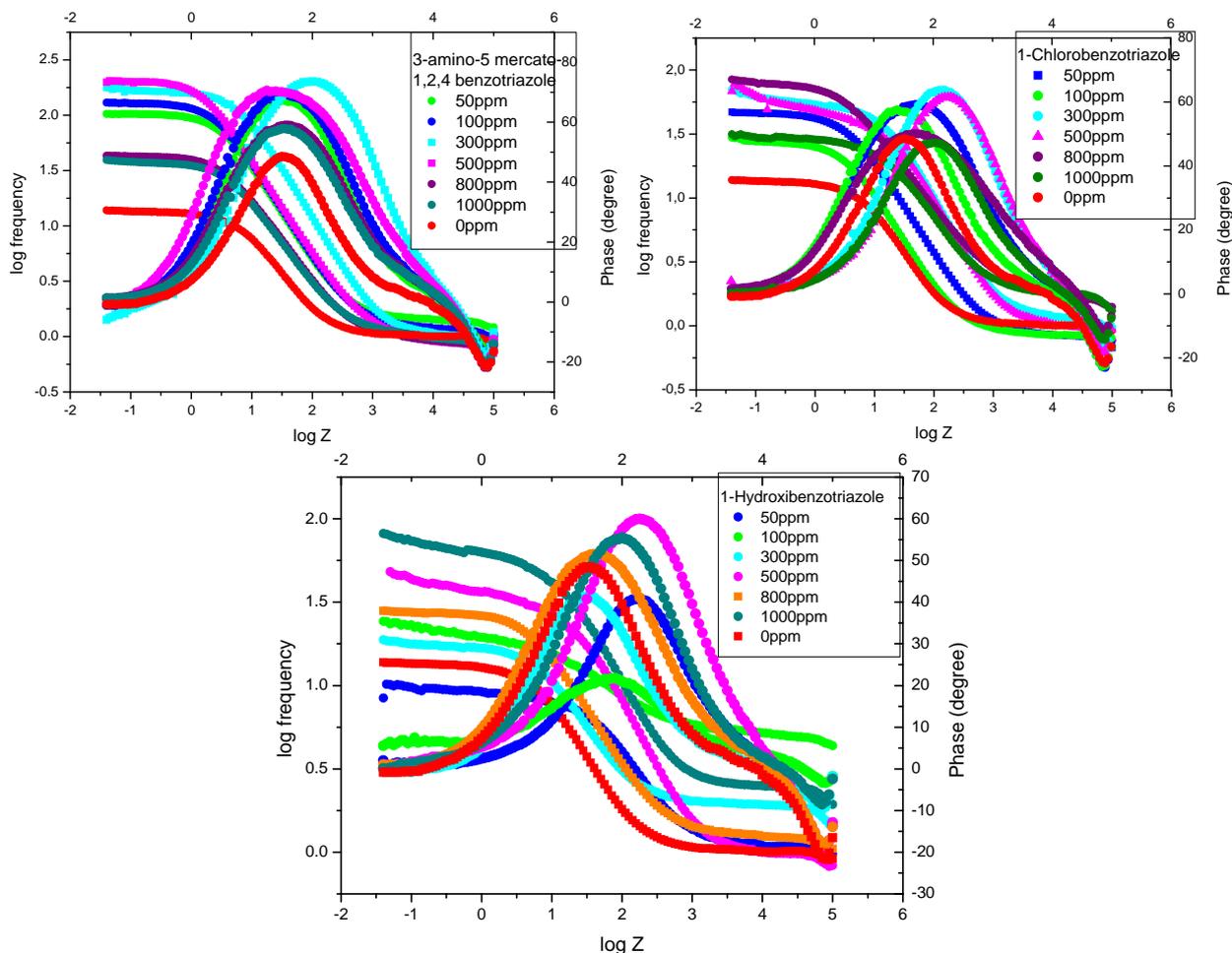


Fig. 7 – The Bode plot for OL37 in 0.5M H₂SO₄ with and without organic inhibitor.

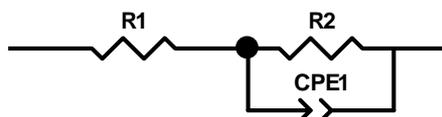


Fig. 8 – Equivalent circuit.

In order to investigate the adsorption behaviour of inhibitor on the surface of carbon steel, spectrometer Bruker optic with ATR was used to measure the spectra of the corroded surface of OL 37 in 0.5M H₂SO₄ containing organic inhibitors. All spectra in these experiments were obtained at a resolution 4 cm⁻¹ in the region 650- 4000 cm⁻¹.

Figs. 9-11 show the FTIR spectra of 5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 mercato-1,2,4 benzotriazole and the corrosion surface of carbon steel in 0.5M H₂SO₄ in presence of these inhibitors.

A transmission vibrational spectrum of 1-Hydroxybenzotriazole is depicted in Fig. 9a. The band in the region from 3545 to 3138 cm⁻¹ is attributed to N-H stretching and that at 3064 cm⁻¹ to C-H. Vibration of benzene ring in heteroaromatic

compound gives rise to absorption bands at 1615 and 1469 cm⁻¹, the band at 1450 is due the vibration of heteroaromatic ring. The band at 1318 cm⁻¹ is attributed to C-N stretching.

The transmission FT-IR spectra obtained for carbon steel type OL37; immersed in 0.5M H₂SO₄ containing 1000 ppm 1-Hydroxybenzotriazole-organic inhibitor is presented in Fig. 9b. This shows the characteristic bands for that adsorbed 1-Hydroxybenzotriazole on the metal surface. A weak band in the range from 3593 to 3279 cm⁻¹ is due to the protonated amine. The presence of N-N, N=N, C-N and C-H and is indicated by their stretching modes at 1655, 1544, 1317 and 1116 cm⁻¹. For this system an additional band at 680 cm⁻¹, is observed that is characteristic of iron-benzotriazole complex.

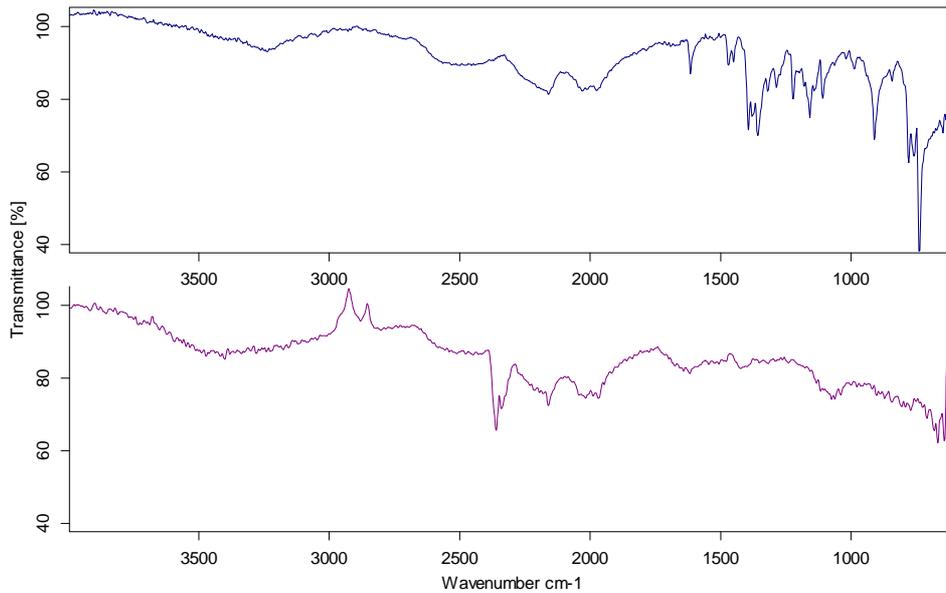


Fig. 9 – FT-IR spectra of (a-blue) 1-Hydroxybenzotriazole (b-purple) OL 37+1000 ppm 1-Hydroxybenzotriazole +0.5M H₂SO₄.

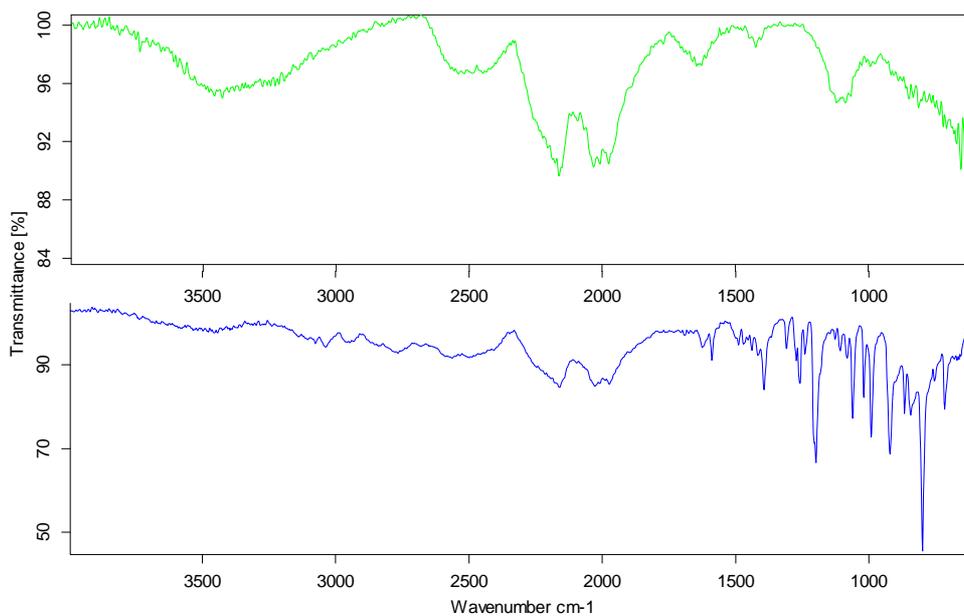


Fig. – 10 FT-IR spectra of (a-blue) 5-Chlorobenzotriazole (b- green) OL 37 +500ppm 5-Chlorobenzotriazole +0.5M H₂SO₄.

The FTIR spectra of 5-Chlorobenzotriazole are shown in Fig. 10a, a peak at 1624 cm^{-1} indicates presence C=N bond and the appearance of a very weak band in the region of 3352 cm^{-1} corresponds to the OH stretching vibration. The presence of C-N and C-H stretching frequencies are clearly manifest in the region 1060 cm^{-1} and 1308 cm^{-1} . Further, peaks at $1580\text{-}1488\text{ cm}^{-1}$ can be attributed to the N-N group present in the ring and the C=C ring stretching peak appears at $1439\text{-}1393\text{ cm}^{-1}$. The peak for N-H stretching modes can be seen in the region at $3582\text{-}3075\text{ cm}^{-1}$. The transmission FT-IR spectra obtained for carbon steel type OL37

immersed in $0.5\text{M H}_2\text{SO}_4$ containing 500 ppm 5-Chlorobenzotriazole organic inhibitor is presented in Fig. 10b. This shows the characteristic bands for that adsorbed 5-Chlorobenzotriazole on the metal surface. A weak band in the range from $3567\text{ to }3265\text{ cm}^{-1}$ can be assigned to the presence of N-H. The presence of C=N, N-N, C=C, C-N and C-H and is indicated by their stretching modes at $1626, 1422, 1383, 1066$ and 1112 cm^{-1} . The bands 3820 cm^{-1} and 3736 cm^{-1} are attributed to Fe-O bending. This is already confirmed from the Langmuir adsorption isotherm studies.

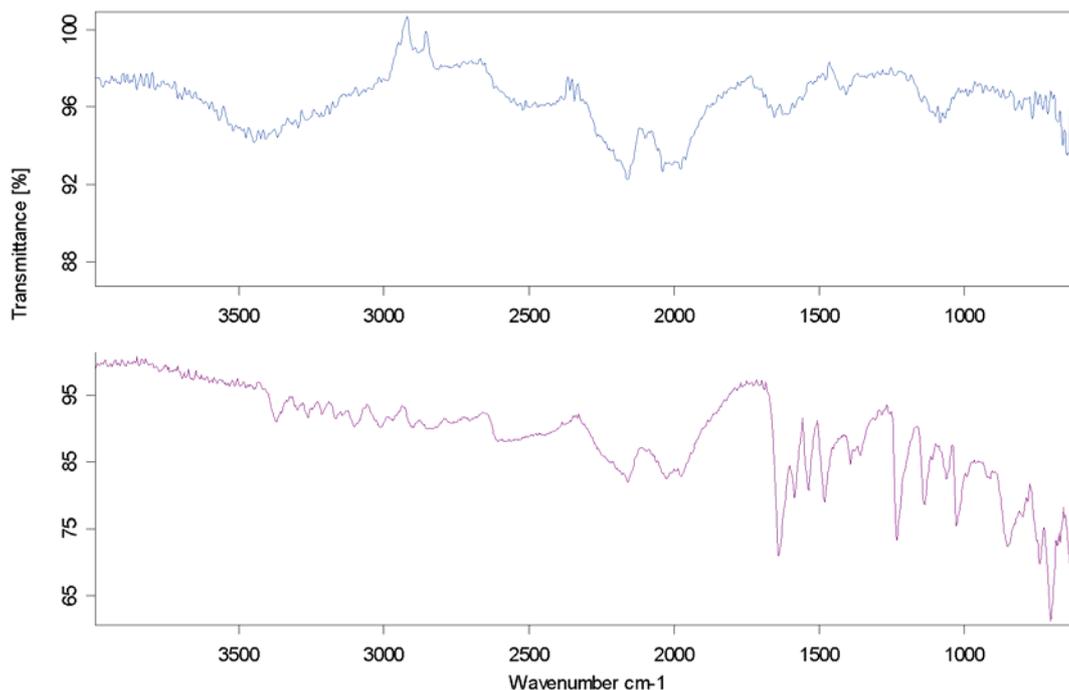


Fig. 11 – FT-IR spectra of (a-purple) 3-amino-5 mercato-1,2,4 benzotriazole (b-blue) OL 37 +100ppm 3-amino-5 mercato-1,2,4 benzotriazole +0.5M H₂SO₄.

FT-IR spectra of 3-amino-5 mercato-1,2,4 benzotriazole are presented in Fig. 11a and FT-IR spectra obtained for carbon steel type OL37 immersed in 0.5M H₂SO₄ containing 100ppm 3-amino-5 mercato-1,2,4 benzotriazole organic inhibitor is presented in Fig. 11b. From Fig. 11a, N-H stretching vibration exhibits absorption in the region 3372 to 3103 cm⁻¹, C-H stretching vibration in benzene ring shows the absorption at 3014 and 1137 cm⁻¹, C-N exhibits at 1377 cm⁻¹. Furthermore, peaks at 1584-1481cm⁻¹ can be attributed to the N-N group present in the ring and the C=C ring stretching peak appears at 1477-1358 cm⁻¹ and the C=N stretching vibration at 1639 cm⁻¹. The presence of S-C and S-H stretching frequencies is clearly manifest in the region 2899 and 2260 cm⁻¹. From figure 11b, it shows the characteristic bands for that adsorbed 3-amino-5 mercato-1,2,4 benzotriazole on the metal surface: the broader band around in the range from 3567 to 35195 cm⁻¹ can be assigned to the presence of N-H. The presence of C=N, N-N, C=C, C-N and C-H and is indicated by their stretching modes at 1654, 1558, 1407, 1083 and 1147 cm⁻¹. The presence of S-C and S-H stretching frequencies is clearly manifest in the region 2932 and 2563 cm⁻¹. Moreover, these FT-IR measurements indicated at 3664 cm⁻¹ the direct bonding between Fe atoms and 3-amino-5

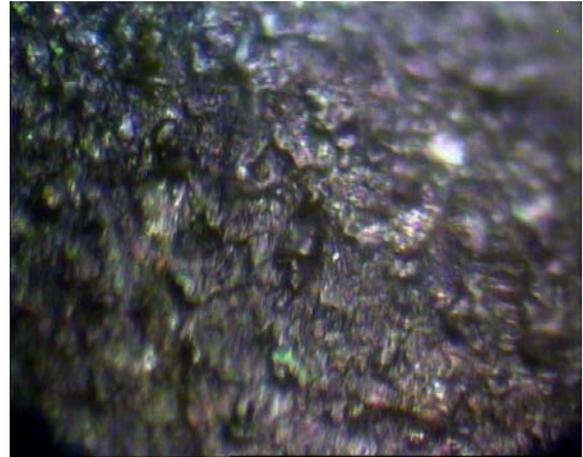
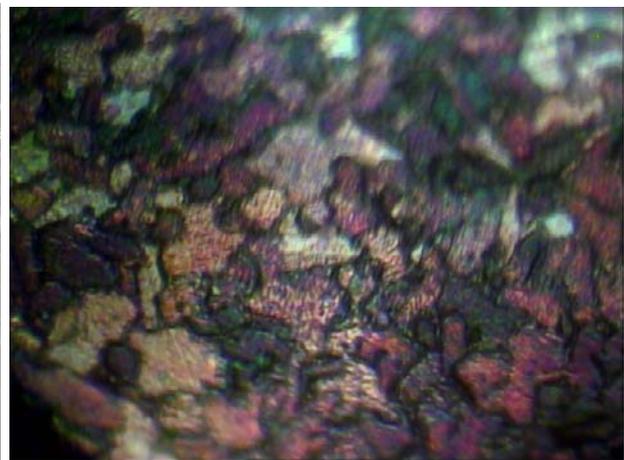
mercato-1,2,4 benzotriazole molecules via O and N atoms, and the formation Fe-inhibitor complex and this reveal that there is only chemical adsorption occurred on the surface of the metal.²⁵⁻²⁸ Comparing Fig. 9a and b, Fig. 10a and b, Fig. 11a and b, it can be observed that the benzotriazole derivatives can be adsorbed on the carbon steel type OL37 surface.

The formation of the protective surface film of organic inhibitor on the electrode surface was confirmed by metallurgical research microscope observation on the electrode surface. Fig. 12 shows a few micrographies obtained by us for the following systems OL 37+0.5M H₂SO₄ and after a certain immersion in H₂SO₄ with and without organic inhibitor. As well in the presence of Xppm organic inhibitors the surface becomes more smooth and homogeneous. Analyzing in comparison Figs. 12b, 12c, 12d and 12e-f, it can be observed that, on the surface of micrographies there are the adsorbed films of inhibitor and corrosion products.

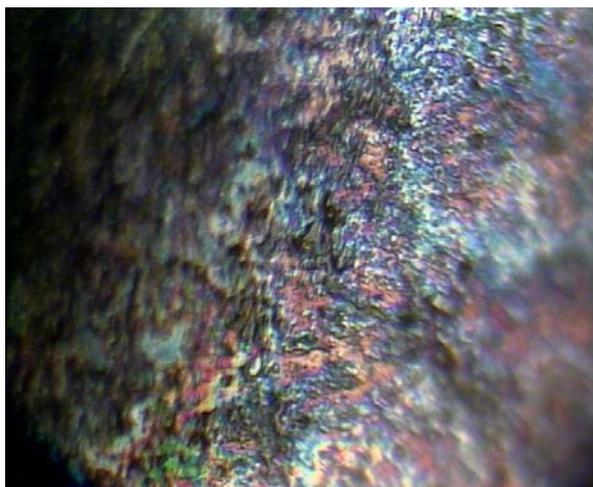
Fig. 12 clearly shows the corrosion degree of carbon steel decreases in the presence of organic inhibitors. These films behave like a barrier between corrosive medium and metal surface and as a consequence the corrosion process is inhibited – see in comparison Fig. 12 (a, b, c, d, e and f).²⁹⁻³¹



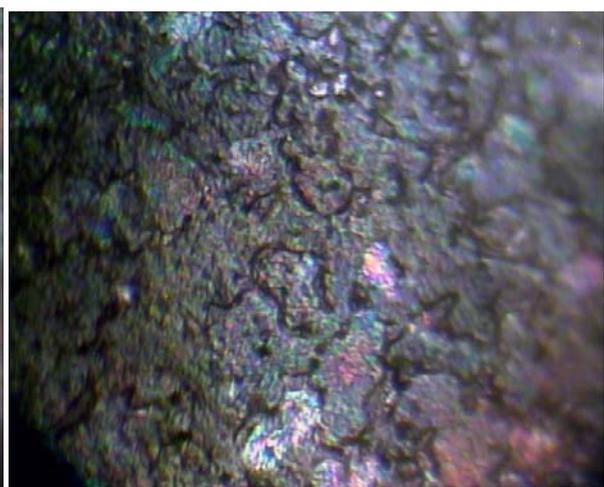
a) OL 37 polished

b) OL37+H₂SO₄c)
OL37-0.5MH₂SO₄+300ppm and 500ppm 3-amino-5 mercato-1,2,4 benzotriazole

d)



e)



f)

OL37-0.5MH₂SO₄+500ppm 5-Chlorobenzotriazole 1000ppm 1-Hydroxy-benzotriazole

Fig. 12 – Micrographies of the carbon steel in 0.5M H₂SO₄ with organic inhibitor: a) OL 37 polished, b) OL37+0.5M H₂SO₄, c) 300ppm 3-amino-5 mercato-1,2,4 benzotriazole d) 500ppm 3-amino-5 mercato-1,2,4 benzotriazole, e) 500ppm 5-Chlorobenzotriazole and f) 1000ppm 1-Hydroxy-benzotriazole.

CONCLUSIONS

The organic inhibitors 5-Chlorobenzotriazole, 1-Hydroxy-benzotriazole and 3-amino-5 mercato-1,2,4 benzotriazole which was obtained by us has presented a good inhibitory action and a significant efficiency for decreasing of the rate corrosion of the studied carbon steel type OL 37 in 0.5M H₂SO₄.

The organic inhibitors were adsorbed on the carbon steel surface according to a Langmuir isotherm. The inhibition activity analysis of the organic compound was made by assuming that the mechanism of inhibition by organic molecules is chemisorption.

FT-IR spectra revealed very clear that these organic inhibitors were adsorbed on the metal surface.

The adsorption of investigated organic inhibitor follows the Langmuir isotherm and the FT-IR results and it also reveals the adsorption of inhibitor molecule on the metal surface and blocking the active sites.

EIS results are in very good concordance with results obtained by potentiodynamic and potentiostatic methods.

The inhibition efficiency follows the order: 5-Chlorobenzotriazole > 3-amino-5 mercato-1, 2, 4 benzotriazole > 1-Hydroxy-benzotriazole

REFERENCES

- J. L. Rozenfeld, "Corrosion Inhibitors", McGraw-Hill, New York, 1981, p. 109.
- D. Jones, "Principle and Prevention of Corrosion", MacMillan Publishing Company, New York, 1992.
- H. H. Uhlig and R. W. Revie, "Corrosion and Corrosion Control", Wiley, New York, 3rd edition, 1985.
- A. S.Fouda, H. A. Mostafa, F. E. Heakal, *Corros. Sci.*, **2005**, *47*, 1988.
- V. Branzoi, and F. Branzoi, *Rev. Roum. Chim.*, **2002**, *47*, 1193-1203.
- V. Branzoi, F. Branzoi and L. Pilan, *Molec. Crystal & Liquid Crystals*, **2006**, *446*, 305.
- M. Lebrini, F. Bentiss, H. Vezin and M. Lagrenee, *Corros. Sci.*, **2006**, *1279*.
- V. Branzoi, F. Branzoi and L. Pilan, *Mater. Chem. Phys.*, **2009**, *118*, 197.
- V. Branzoi, A. Pruna and F. Branzoi, *Rev. Roum. Chim.*, **2007**, *52*, 587.
- A. K. Singh and M. A. Quraishi, *Corros. Sci. Acta*, **2010**, *52*, 152.
- K. C. Emregul, E. Duzgun and O. Atakol., *Corros. Sci.*, **2006**, *86*, 3487.
- E. Kamis, F. Bellucci, R. M. Latonision and E. S. H. El-Ashry, *Corrosion*, **1991**, *47*, 677.
- M. Beier and J. W. Schultze, *Electrochim. Acta*, **1992**, *37*, 2299.
- J. Aljourani, K. Raeissini and M. A. Golozar, *Corros. Sci.*, **2009**, *51*, 1836
- Y. A. Aleksanyan, I. I. Reformatskaya and A. N. Podobaev, *Protection of Metals*, **2007**, *43*, 125.
- E. M. Sherif and S.-M. Park, *Electrochimica Acta*, **2006**, *51*, 4665-4673.
- L. Wang, *Corros. Sci.*, **2006**, *48*, 608.
- F. Mansfeld, "Corrosion Mechanism", Marcel Dekker (Ed.), New York, 1987, p. 119.
- S. M. A. Hosseini and A. Azimi, *Mater. Corros.*, **2008**, *59*, 41.
- E. M. Sherif, *J. Appl. Surf. Sci.*, **2006**, *252*, 8615.
- G. B. Hunt and A. K. Holiday, "Organic Chemistry", London, United Kingdom, Buterworth, 1981, p. 229.
- R. D Braun, E. E Lopez and D. P. Vollmer, *Corros. Sci.*, **1993**, *34*, 1251.
- G. Gunasekaran and R. Chauhan, *Electrochim. Acta*, **2004**, *49*, 4387.
- H. A. Loupy, *Chemistry Today*, **2006**, *24*, 36.
- Q. Qu, S. Jiang, W. Bai and L. Li, *Electrochim. Acta*, **2007**, *52*, 6811.
- Q. Quing, L. Li, S. Jing and Z. Ding, *J. Appl. Electrochem.*, **2009**, *39*, 569.
- M. F. L. Granero, P. H. L. S. Matai, I. V. Aoki and I. C. Guedes, *J. Appl. Electrochem.*, **2009**, *39*, 1199.
- D. Gopi, K. M. Govindaraju and L. Kavitha, *J. Appl. Electrochem.*, **2010**, *40*, 1349.
- A. Prună, V. Branzoi and F. Branzoi, *Materials and Technologies*, **2007**, *23*, 233.
- V. Branzoi, F. Branzoi and I. Harabor, *Rev. Roum. Chim.*, **2010**, *55*, 48.
- F. Branzoi and V. Branzoi, *Rev. Roum. Chim.*, **2013**, *58*, 747.