

## A NEW INHIBITOR FOR CORROSION OF CARBON STEEL IN HYDROCHLORIC ACID SOLUTION

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The corrosion and inhibition behavior of carbon steel in 1M HCl in the presence of Bis (2-Benzothiazolyl) disulphide (BTD) was investigated using weight loss measurements, electrochemical measurements and UV-VIS spectrophotometry. The morphology of carbon steel surface was investigated by using microscopic analysis and Mössbauer spectrometry. The corrosion current was determined by using Tafel polarization. The inhibition efficiency increased with BTD concentration and the experimental results suggest that the presence of BTD in the solution increase the surface coverage ( $\theta$ ) and therefore, indicate the adsorption of BTD. The adsorption of this compound on the metal surface obeys Langmuir's adsorption isotherm. Mossbauer spectroscopy shown at this stage the main product of corrosion consists in a mixture of  $\alpha$ ,  $\beta$  and  $\gamma$ -FeOOH, where  $\gamma$ -FeOOH is the main phase. BTD inhibitor acts as an incipient "rust transformer" and favors the formation of a "superficial closed layer". The UV-VIS spectrophotometry shown a decrease of the concentration of BTD in 1M HCl solution after corrosion, indicating that an adsorption process between organic compound from aqueous phase and the electrode surface.

### INTRODUCTION

One of the most aggressive media for the ferric materials is the aqueous solution of hydrochloric acid. The importance of inhibition is much greater in solutions of hydrochloric acid since iron and its alloys are the most exposed materials both in industrial media and other media, while these metallic materials are more susceptible to being attacked in an acid pH medium rather than in an alkaline solutions. One of the most important methods in corrosion protection of metals is the use of organic inhibitors to protect the metal surface from the corrosive media.<sup>1-10</sup> Sulfur compounds have a strong affinity to transition metal surfaces.<sup>11-18</sup> Organic sulfur compounds coordinate very strongly to the surface of the metal. The number of reported surface-active organic sulfur compounds that form monolayers on metal surfaces has increased in recent years. The available results show that most inhibitors act by adsorption on the metal surface.<sup>11-18</sup> The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties

of the layer formed on the metal surface under particular experimental conditions. In order to study the inhibition of organic sulfur compounds in the selected medium, a number of methods can be used. Among the rapid methods of detection are the weight loss measurements and electrochemical measurements. The present study aims to determine the role of new inhibitor Bis (2-Benzothiazolyl) disulphide (BTD) in improving the protection film in case of generalized corrosion of carbon steel in hydrochloric acid using weight loss measurements and electrochemical measurements. The morphology of carbon steel surface was investigated by using scanning electron microscopy (SEM) and Mössbauer spectrometry.

### RESULTS AND DISCUSSION

#### Weight loss measurements

The loss in the weight of carbon steel samples in 1M HCl in absence and presence of various concentrations of BTD was determined. The

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results of weight loss measurements are shown as general corrosion rates,  $k_g$  ( $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) in Fig. 1. The increase in BTD concentrations leads to a decrease in the corrosion rate for both examined samples, indicating that the presence of BTD retards the general corrosion of samples in 1M HCl. This suggests that the inhibition of the carbon steel corrosion in the presence of BTD occurs by adsorption at site on the metal surface. Sulfur compounds have a strong affinity to transition metal surface. Organic sulfur compounds coordinate very strongly to the surface of the carbon steel and they form monolayers on the metal surface. The adsorption of BTD molecules also produces important modifications in the structure of the double electric layer. Electrode/electrolyte interfaces demonstrate a capacitance whose magnitude reflects the distribution of ions on the solution side of the interface. The electrolyte double layer is composed of the Helmholtz layer consisting of ions and solvent in physical contact with the electrode and

the diffuse layer, which contains iron ions near the electrode whose concentrations deviate from bulk concentrations. It seems that complex formation occurs between the BTD compound (as ligand) and different metal cations in the steel. These complexes can form stable passive layer on the steel surface; thus decreasing the rate of corrosion. The effect of surface blockage becomes dominant, which leads to a decrease in the active centres. The inhibition efficiency increases with BTD concentration (Fig. 1). The percentage inhibition efficiency ( $P$ ) of BTD was calculated by applying the following equation:

$$P = \frac{k_{g0} - k_g}{k_{g0}} \cdot 100 \quad (1)$$

where  $k_{g0}$  and  $k_g$  are, respectively, the corrosion rates in the absence and presence of a given inhibitor. The inhibition efficiencies calculated from the weight loss data are given in Fig. 1.

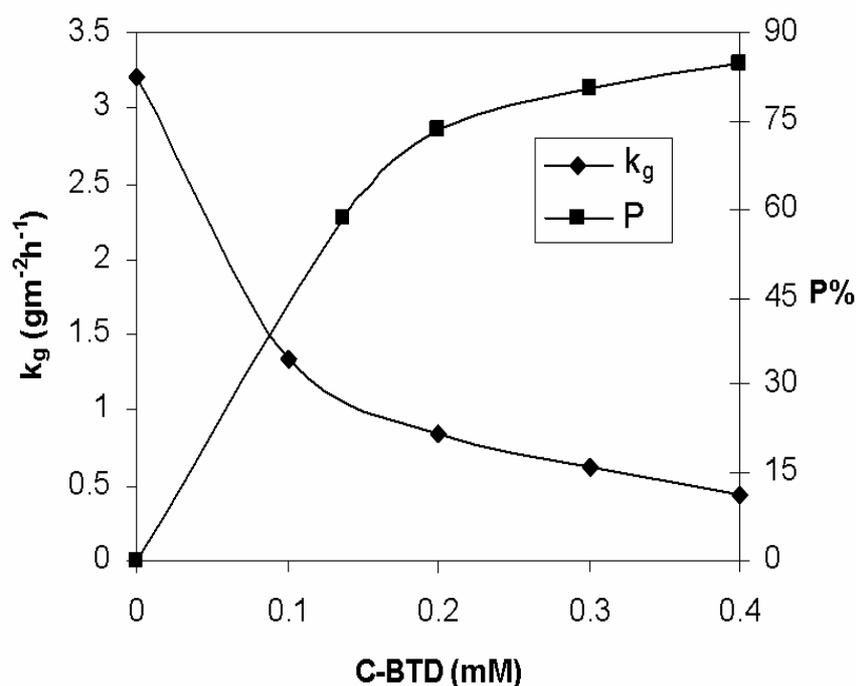


Fig. 1 – Variation of corrosion rate and percentage protection efficiency ( $P$ ) with the concentrations of BTD for the carbon steel in 1M HCl, at room temperature.

On studying the inhibitor we have reached the conclusion that the experimental data characterize an adsorption isotherm of Langmuir type expressed by linearization form (relation 2), as an example in Fig. 2.

$$\frac{c}{\theta} = c + \frac{1}{K} \quad (2)$$

where  $\theta$  is degree of coverage ( $\theta=P/100$ ),  $K$  is the equilibrium constant of the adsorption-desorption process,  $c$  is concentration of the BTD.

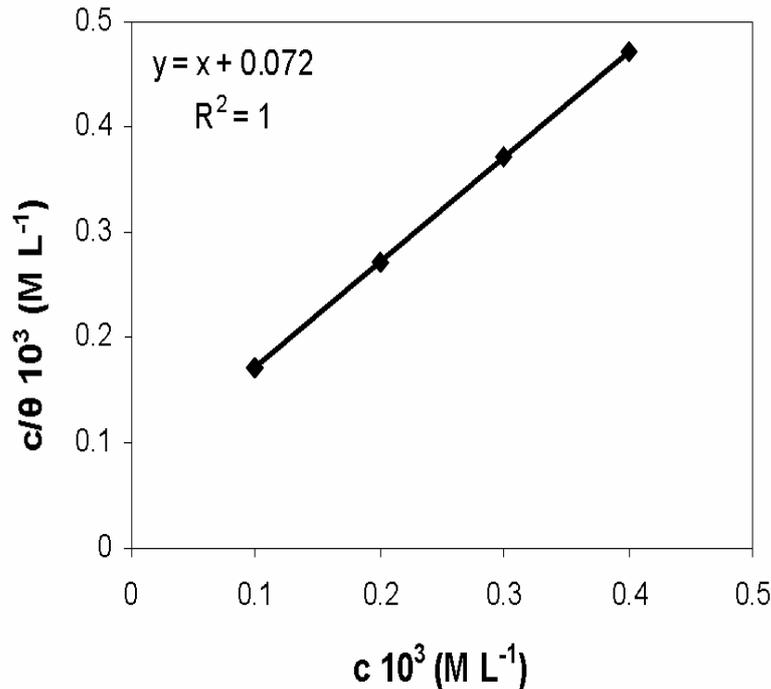


Fig. 2 – The results of a Langmuir diagram in case of corrosion inhibition of carbon steel in a solution of 1M HCl with BTB.

The data gave straight line and the intercept with the ordinate representing  $1/K$ . It can be observed that  $K$  has a high value of  $13800 \text{ M}^{-1} \text{ L}$ . The equilibrium constants  $K$  vary towards the same direction, in the sense that higher values of  $K$  imply a better adsorption. In general sense, we consider that BTB forms a self-assembled monolayers can be defined as well-ordered and oriented molecular film, which are formed spontaneously, upon immersion of carbon steel substrate in the solution containing an active surfactant molecule, as BTB.

The free standard energy of adsorption  $\Delta G_{ads}^0$  was calculated with the relation 3:

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^0}{R \cdot T}\right) \quad (3)$$

where  $R$  is the universal gas constant,  $T$  is temperature (K) and  $55.5$  is the molar concentration of water in the solution.

The value of  $\Delta G_{ads}^0$  is negative ( $-32.96 \text{ kJ} \cdot \text{mol}^{-1}$ ), which shows that the process of adsorption is spontaneous.

The morphology of carbon steel surface after corrosion in 1M HCl solution, in absence of BTB (Fig. 3a) and in 1M HCl solution containing  $0.4 \text{ mM}$  BTB (Fig. 3b) was examined with an electronic microscope (VEGA TESCAN).

Fig. 3 shows the evidence of formation a protective film on the surface of carbon steel. The corrosion spots are reduced in intensity in the case of carbon steel corroded in 1M HCl containing  $0.4 \text{ mM}$  BTB (Fig. 3b). It can be concluded that the inhibitor molecules are adsorbed on the carbon steel surface.

### Electrochemical measurements

Fig. 4 shows the polarization curves of carbon steel in 1M HCl blank solution and in the presence of various concentrations of BTB.

The increase in BTB concentrations lead to both anodic and cathodic current inhibition, but the reduction in the anodic current was more significant than that of the cathodic current. This shows that the addition of BTB reduces anodic dissolution and also retards the hydrogen evolution reaction. The presence of a benzothiazolic rings and S-atoms in a BTB molecule can enhance the binding between carbon steel surface and organic compound, which consequently results in the formation of compact and impermeable self-assembled monolayer. BTB self assembled - monolayer restrain faradaic processes such as electrode oxidation and the exchange of electrons between the electrode and solution redox couples. The property of this blocking is attributed to the

compactly packed structure of the monolayer, which obstructs the approach of solution  $\text{Cl}^-$  ions to the electrode surface. The corrosion current was

calculated at intercept of the anodic and cathodic Tafel lines resolving the system of equations which are presented in Fig. 5, for each solution.

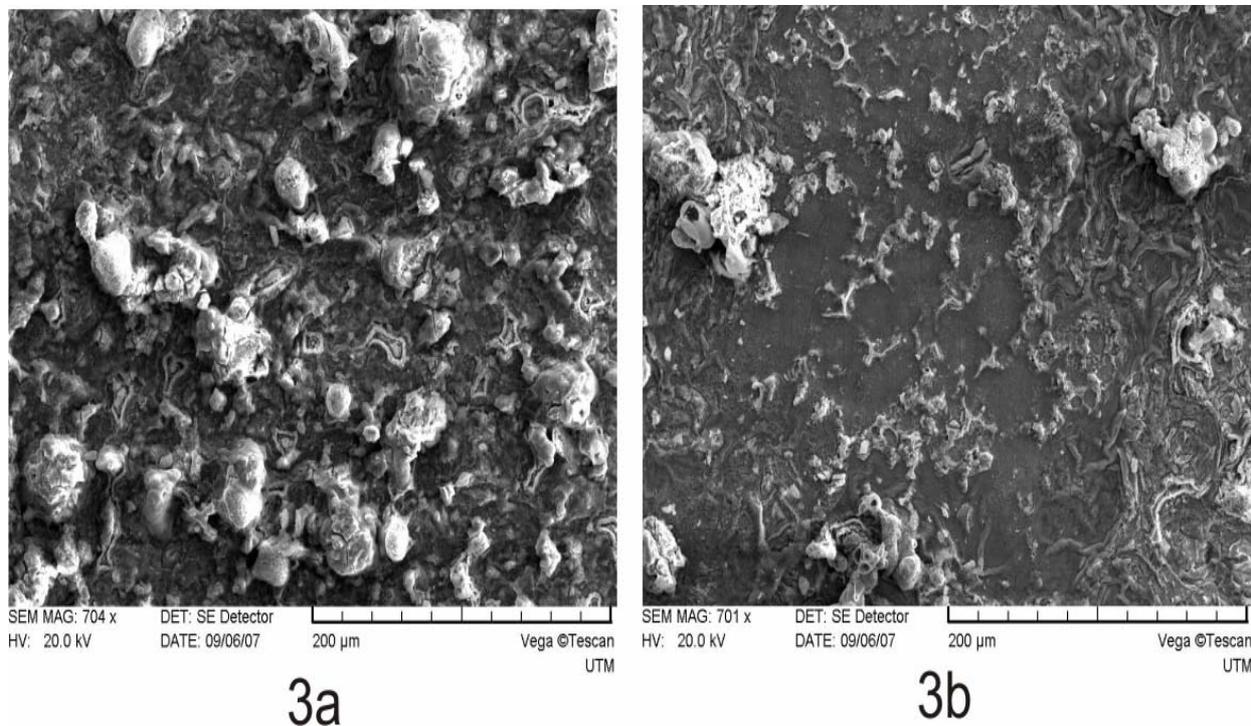


Fig. 3 – The electrode surface microscopically analysed after corrosion in: (a) 1M HCl solution; (b) 1M HCl with 0.4 mM BTM.

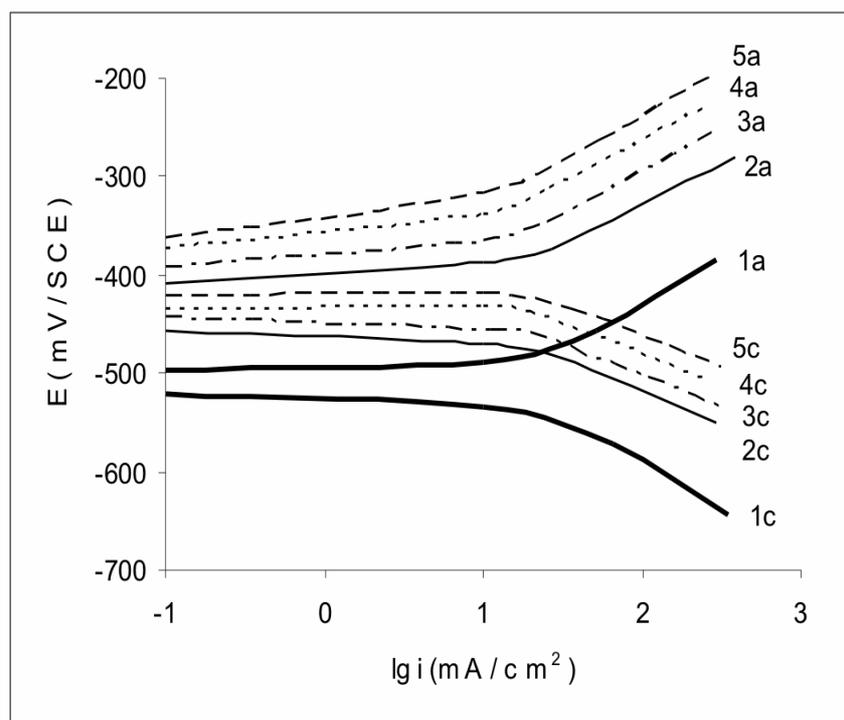


Fig. 4 – The polarization curves of carbon steel in 1M HCl solution in absence and in the presence of BTM with various concentrations: 1-blank; 2-0.1mM; 3-0.2mM; 4-0.3mM; 5-0.4mM; anodic and cathodic denoted by “a” and “c” respectively.

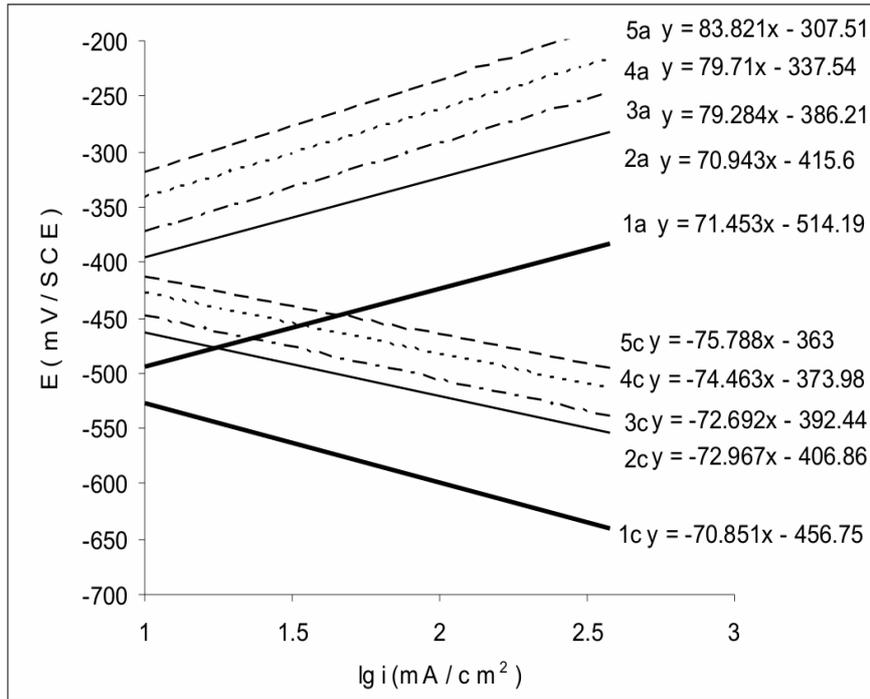


Fig. 5 – Tafel diagram of carbon steel in 1M HCl solution in absence and in the presence of BTD with various concentrations: 1-blank; 2-0.1mM; 3-0.2mM; 4-0.3mM; 5-0.4mM; anodic and cathodic denoted by “a” and “c” respectively.

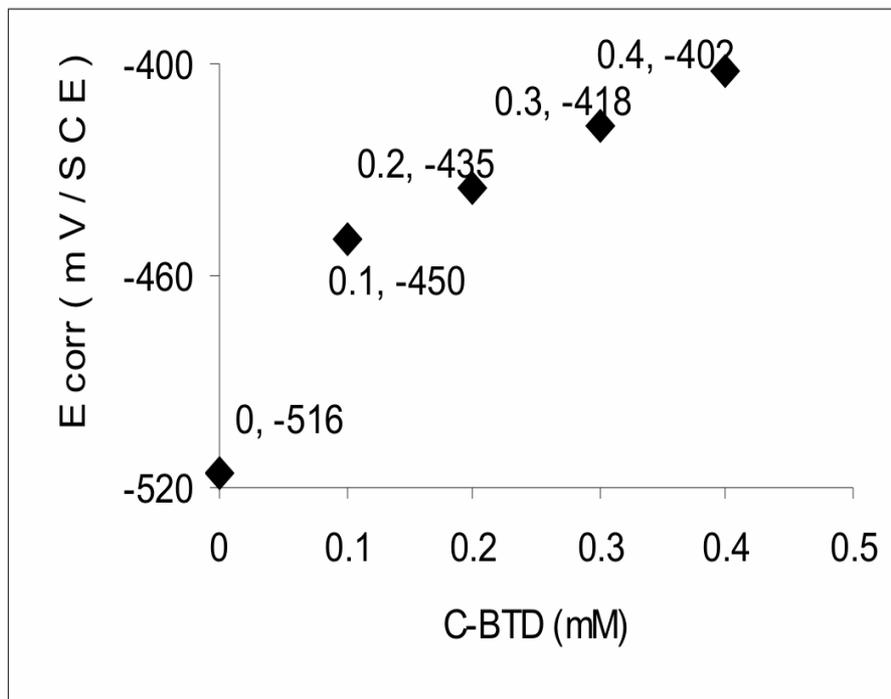


Fig. 6 – Dependence of  $E_{corr}$  of carbon steel in 1M HCl solution in absence and in the presence of BTD on inhibitor concentration.

Decrease of the corrosion current ( $i_{corr}$ ) was associated with a shift of corrosion potential ( $E_{corr}$ ) to a less negative values (Fig. 6). This suggests that

although inhibition is of mixed type, it is predominantly anodic.

It can be concluded that the  $E_{corr}$  values are shifted positively; the  $i_{corr}$  values decrease in the presence of various concentration of BTD; Tafel lines of nearly equal slopes  $-dE/d(\lg i)$  were obtained (Fig. 5). This indicates that the adsorbed molecules of BTD do not affect the mechanism of iron dissolution or hydrogen evolution. The percentage inhibition efficiency (P) of BTD inhibitor was also determined from the polarization measurements according to the following equation:

$$P = \frac{i'_{corr} - i_{corr}}{i'_{corr}} \times 100 \quad (6)$$

$i'_{corr}$  and  $i_{corr}$  are the uninhibited and inhibited corrosion current density, respectively obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential.

The values of inhibition efficiency increase with BTD concentration reaching a maximum value of 82.2% at 0.4 mM, nearly equal than the value obtained from loss weight data, 84.7%. Fig. 7 gives the values of corrosion current and inhibition efficiency for the corrosion of carbon steel in 1M HCl solution, with different concentrations of BTD.

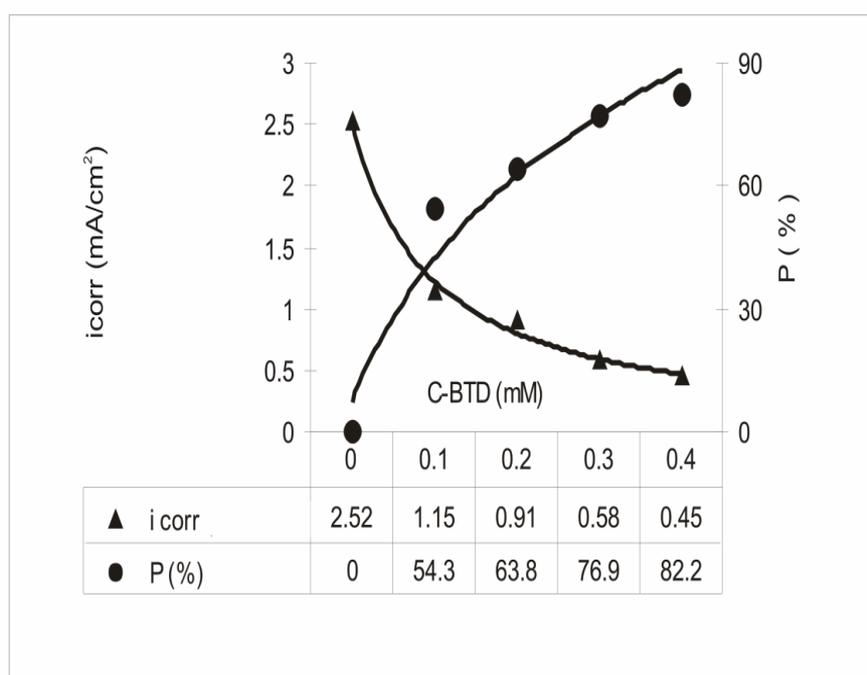


Fig. 7 – Values of corrosion current and inhibition efficiency for the carbon steel in 1M HCl solution blank and with different concentrations of BTD.

### Mössbauer Spectroscopy

The transmission (TMS) and conversion electron (CEMS) spectra of a reference sample before corrosion process (uncorroded sample) are the same with those reported in previous study of authors.<sup>19</sup> The best fitting of the TMS spectrum shows the presence of a single sextet. The parameters of this sextet are the same as for a  $\alpha$ -Fe sample. The full width at half-height of the outermost lines ( $0.3 \text{ mm/s} \pm 0.01$ ) confirms the low concentration of alloying elements given by chemical analysis. The CEMS spectrum shows the presence of the same  $\alpha$ -Fe. In the CEMS spectrum of the reference sample the intensities of the

second and fifth peaks of the  $\alpha$ -Fe spectrum as compared to the third and fourth peaks (3:3.6:1) show that the directions of the  $\gamma$ -ray and the magnetic moments are nearly perpendicular. There is a magnetic anisotropy on the surface of the samples, obtained, mainly, by polish procedure. In contrast TMS spectrum shows that in the interior of the sample the magnetic moments are in a random arrangement. The line width of the CEMS spectrum is  $0.27 \text{ mm/s} \pm 0.02$ . The smaller line width is expected in the backscattering geometry due to lack of saturation broadening.

The CEMS spectra of the sample corroded in 1M HCl solution without BTD and in 1M HCl solution with BTD are shown in Fig. 8 and Fig. 9.

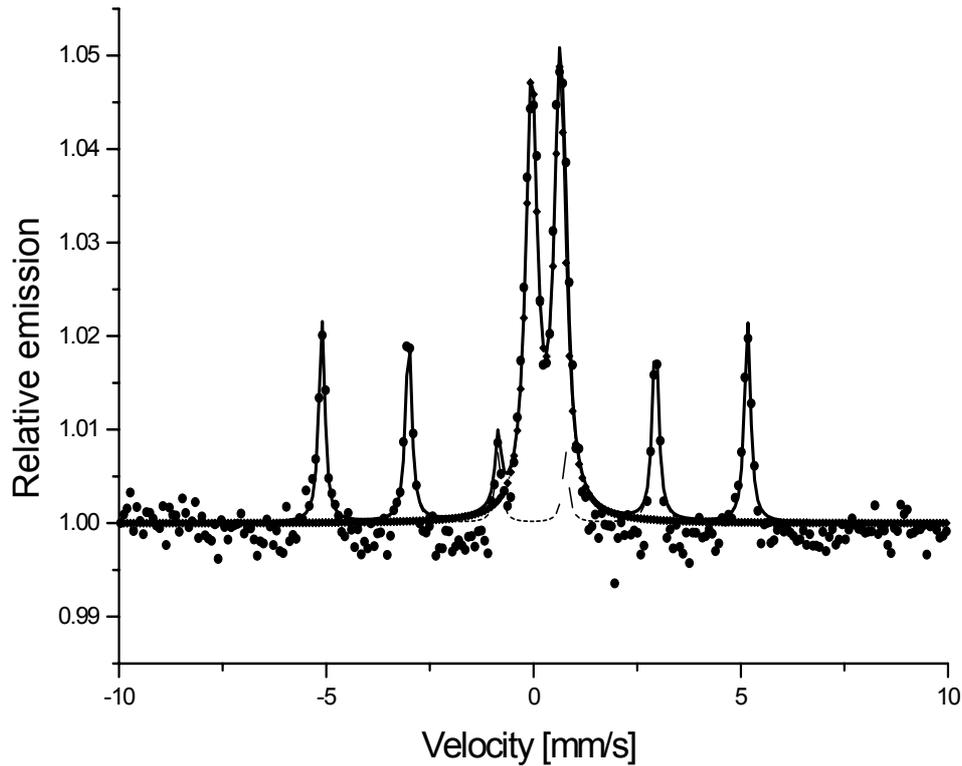


Fig. 8 – Conversion electron Mossbauer spectrum of the Fe-C steel sample with low C concentration after corrosion in a HCl solution (• data; — fit; - -  $\alpha$ -iron; —◆—  $\text{Fe}^{3+}$ ).

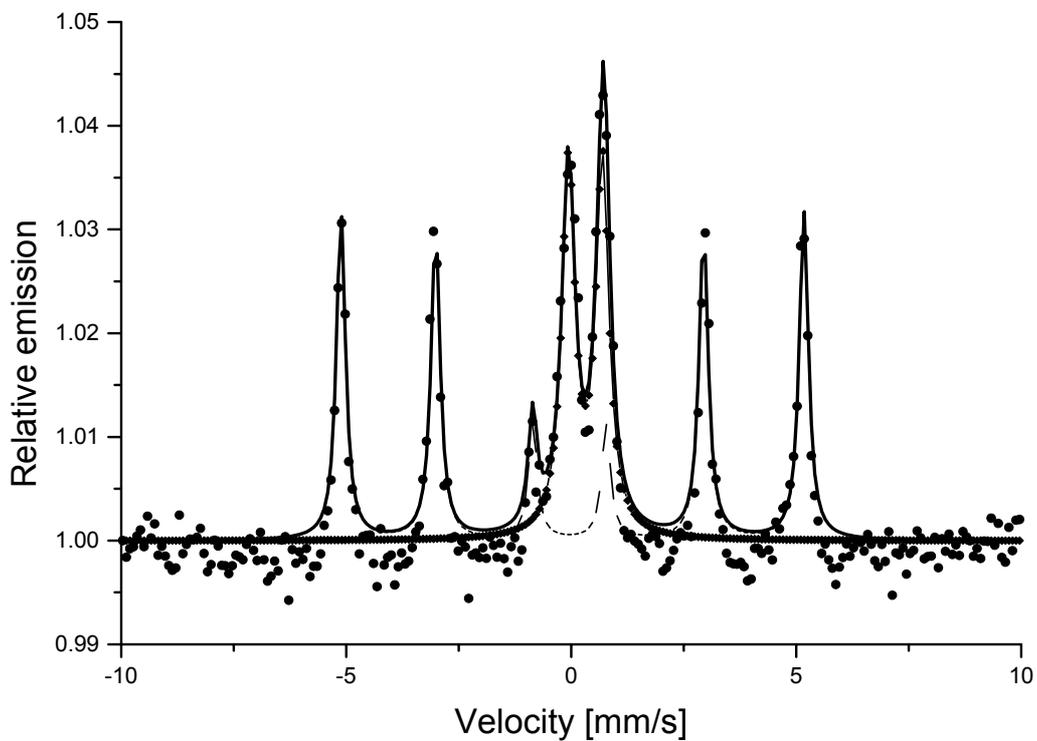


Fig. 9 – Conversion electron Mossbauer spectrum of the Fe-C steel sample with low C concentration after corrosion in a HCl solution with BTDA inhibitor (• data; — fit; - -  $\alpha$ -iron; —◆—  $\text{Fe}^{3+}$ ).

The best fit of the CEMS spectra for the corroded samples uses addition of  $\text{Fe}^{3+}$  paramagnetic doublet

to the sextet. The Mössbauer data obtained by fitting process are given in Table 1.

Table 1

The main Mössbauer parameters of the surface layers

Sample	Sextet							Doublet				
	IS	QS	H	$\epsilon$	W	A	Lines area report	IS	QS	$\epsilon$	W	A
Reference sample	0.00	0.01	332.2	3.13	0.27	100	3:3.6:1					
Sample in 1M HCl solution	0.03	0.03	332	2.18	0.28	35.79	3:2.7:1	0.35	0.71	4.63	0.35	64.21
Sample in 1M HCl solution with BTB	0.03	0.03	332.4	3.17	0.25	58.07	3:3.1:1	0.37	0.78	3.59	0.50	41.93

where: IS Isomer shift in mm/s; errors  $\pm 0.02$

QS Quadrupole splitting in mm/s; errors  $\pm 0.03$

H Hyperfine magnetic field in Koe; errors  $\pm 3$

$\epsilon$  Resonance effect in %; errors  $\pm 0.05$

W Line width in mm/s; errors  $\pm 0.02$

A Relative area of a subspectrum in %; errors  $\pm 5$

The parameters of the sextet (hyperfine magnetic field, quadruple splitting, isomer shift) of the corroded sample except line width and resonance effect are identically to those of the non-corroded sample. The line with increase slightly for the corroded samples, mainly for the sample immersed in solution without inhibitor. This suggests that in the process of corrosion there is a possible preference in depth for the some positions of iron. The presence of the inhibitor stops this preference. The preferential orientation of the magnetic moments in the sample plane continues to exist even after the corrosion of the samples. This preferential orientation is more evidently for sample corroded in 1M HCl solution with BTB (3:3.1:1) compared with the sample corroded in HCl solution without inhibitor (3:2.7:1).

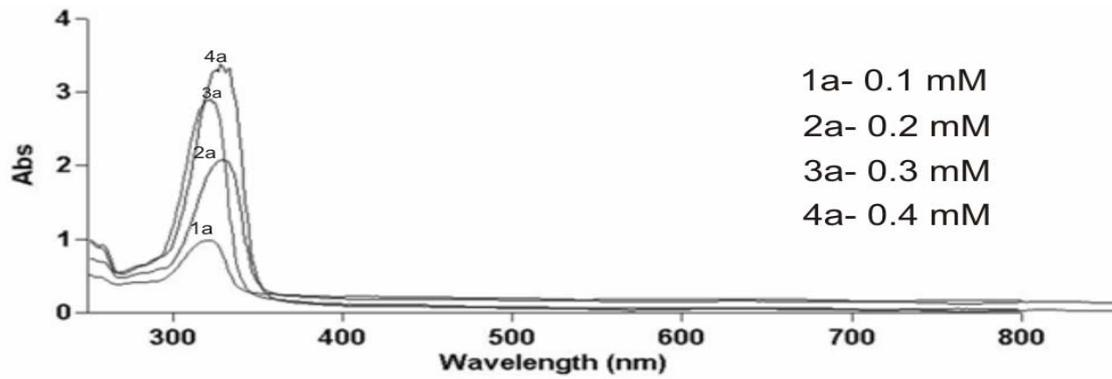
This means that the depth of the corroded surface layer is lower in the inhibitor presence and proves the inhibition action of the BTB inhibitor. The main difference between the corroded sample sextets and the non-corroded sextets consists in the decrease of the intensity lines. This decrease is higher for the sample corroded in HCl solution. This demonstrates the presence of a superficial layer on the corroded samples surface, reconfirming the formation of a superficial compound, without magnetic ordering, as a result of corrosion and inhibition action. The deep of the compound is higher on the corroded sample surface in solution without inhibitor.

The doublet parameters for the corroded sample in solution without inhibitor show the presence of  $\text{Fe}^{3+}$  species and are similar to those shown by amorphous  $\text{Fe}^{3+}$  oxyhydroxides, superparamagnetic  $\alpha$ - $\text{FeOOH}$  and/or  $\gamma$ - $\text{FeOOH}$ ,  $\beta$ - $\text{FeOOH}$ ,  $\beta$ - $\text{FeOOH}$  and  $\gamma$ - $\text{FeOOH}$  and  $\text{Fe}(\text{OH})_3$ . At this stage it is expected that the main product of corrosion is a non-stoichiometric amorphous  $\text{Fe}^{3+}$  oxyhydroxide, consisting of a mixture of  $\alpha$ ,  $\beta$  and  $\gamma$ - $\text{FeOOH}$ , where  $\gamma$ - $\text{FeOOH}$  is the main phase.<sup>20-28</sup> Evidence has been provided for  $\beta$ - $\text{FeOOH}$  formation as a result of Fe and carbon steel oxidation in the presence of Cl ions.

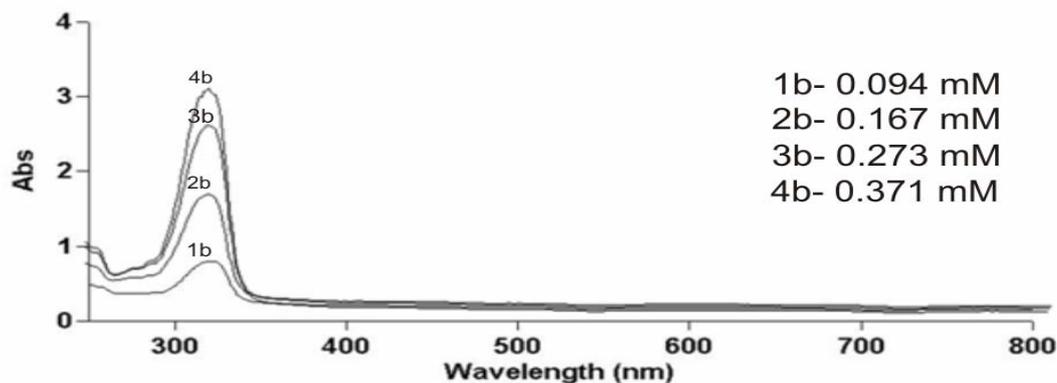
In the case of the corroded samples in a solution of 1M HCl containing of BTB the process of corrosion is considerable slowed and a superficial compound of  $\text{Fe}^{3+}$  without a magnetic arrangement is formed. By estimating its relative area, this compound has a smaller thickness than the layer formed in the corrosion process without inhibitor. The Mössbauer parameters of the compound in this case do not differ significantly from the ones found for the corroded sample in the solution without inhibitor. The new parameters can be ascribed to above superficial compound as well as ferrihydrites. It is known that ferrihydrite is a precursor of other ordered oxyhydroxides. We consider that the BTB inhibitor acts as an incipient "rust transformer" and favours the formation of a "superficial closed layer". The inhibitor transform some constituents of rust into corrosion inhibiting oxide phases.

### UV-VIS spectrophotometry

Fig. 10 shows the UV-VIS spectra of BTB at different concentrations in 1M HCl solutions, before and after carbon steel corrosion in these media.



A. Before corrosion of carbon steel in these media



B. After corrosion of carbon steel in these media

Fig. 10 – UV-VIS spectra of BTBD of various concentrations in 1M HCl solution A. Before corrosion of carbon steel in these media, B. After corrosion of carbon steel in these media.

It was observed that in all the cases the concentration of BTBD decreases after corrosion of carbon steel in 1M HCl solution with various

concentrations of BTBD (Table 2). This indicates that the molecules of BTBD from aqueous phase were adsorbed on the surface of the electrode.

Table 2

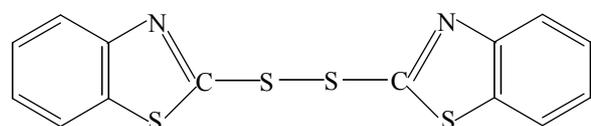
The concentrations of BTBD in 1M HCl before and after corrosion of carbon steel in these media

$\lambda$ (nm)-314				
<b>before corrosion</b>				
Absorbance	0.671	1.667	2.930	3.366
C-BTD (mM)	0.1	0.2	0.3	0.4
<b>after corrosion</b>				
Absorbance	0.636	1.479	2.787	3.093
C-BTD (mM)	0.094	0.167	0.273	0.371

## EXPERIMENTAL PART

The carbon steel used had the following composition (weight %): C=0.1%; Si=0.035%; Mn=0.4%; Cr=0.3%; Ni=0.3%, with the balance in Fe. The samples were mechanically polished with different grades of emery paper (down to 600), degreased with acetone and dried. 1M HCl acid was used as the blank corrosion test solution.

The inhibitor used was Bis (2-Benzothiazolyl) disulphide (BTBD) in concentrations of 0.1 mM; 0.2 mM; 0.3 mM; 0.4 mM; it has following chemical structure:



### Weight loss measurements

The corrosion rates of carbon steel were determined in HCl 1M solution in the absence and presence of some variable concentrations of BTB: 0.1 mM; 0.2 mM; 0.3 mM; 0.4 mM. The immersion time of the plates in the respective media was three hours, at room temperature. The morphology of carbon steel surface after corrosion in 1M HCl solution and 1M HCl solution containing 0.4 mM BTB was examined with an electronic microscope (VEGA TESCAN).

### Electrochemical measurements

For the study of polarization a standard corrosion cell was used, with a working electrode made of carbon steel with an active surface of 4 cm<sup>2</sup>. The saturated calomel electrode (SCE) was used as a reference electrode. The auxiliary electrode was a carbon steel plate identical to the one used as the working electrode. The polarization was conducted in an electrochemical system Keithley 2420 3A Source Metter with a personal computer and Test Point software, at room temperature. Five determinations were made for each solution, taking into consideration the most reproducible responses for the same current densities; error associated with the inhibition was 2±0.5%.

### Mössbauer Spectrometry

Mössbauer spectrometry measurements were performed at room temperature in the transmission (TMS) and conversion electron spectroscopy (CEMS) using constant-acceleration spectrometer with a <sup>57</sup>Co - Rh Source. The CEMS measurement, effected with our CEMS detector<sup>29,30</sup> were conducted to a high degree of accuracy, ensuring the same geometry of the detection space and same gas flow rate for all the samples. The parameters of the Mössbauer spectra were calculated using a computer – fitting program, which assumes a Lorentzian line shape. The isomer shifts were referred to  $\alpha$ - Fe. The information obtained by scattering methods is restricted to the layer to which the secondary radiation employed in the measurement can penetrate from the surface of the sample. In the <sup>57</sup>Fe Mössbauer spectroscopy the penetration depth maximum of conversion electron is of the order of 250 nm.

### UV-VIS spectrophotometry

The adsorption process of organic compounds from aqueous phase on the electrode surface was demonstrated by using UV-VIS analysis reports of media 1M HCl containing BTB at various concentrations before and after corrosion of carbon steel. In the UV-VIS spectrophotometry was used a spectrophotometer of type VARIAN-CARY 50 (soft-CARY WIN). Procedure: The solutions were placed in the UV-VIS beam and a graph of absorbance versus the wavelength was obtained; for each sample analysis reports were obtained using the soft CARY-WIN UV. Alternatively, the solutions were prepared in known concentrations of BTB and they were read by the UV-VIS spectrophotometer. Results are the graphed to make a calibration curve from which the unknown concentration of BTB can be determined by its absorbance.

## CONCLUSIONS

BTB is an inhibitor of carbon steel in a solution of 1M HCl; it has an efficiency of 84.7% obtained by weight loss measurements respectively 82.2% by electrochemical measurements. The adsorption of BTB on the electrode surface is found to obey Langmuir's adsorption isotherm. The microscopic analysis of the surface of the electrode shows a decrease of the corrosion spots with the increase of the BTB concentration. This indicates a good adsorbability of BTB on the carbon steel surface. Mossbauer spectroscopy shown at this stage the main product of corrosion is a non-stoichiometric amorphous Fe<sup>3+</sup> oxyhydroxide, consisting of a mixture of  $\alpha$ ,  $\beta$  and  $\gamma$ -FeOOH, where  $\gamma$ -FeOOH is the main phase. The authors consider that the BTB inhibitor acts as an incipient "rust transformer" and favours the formation of a "superficial closed layer". The inhibitor transform some constituents of rust into corrosion inhibiting oxide phases. BTB acts through adsorption on the metal surface; it was demonstrated by using loss weight and electrochemical measurements; UV-VIS spectrophotometry confirms the adsorption process of organic compounds from aqueous phase on the electrode surface.

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