*Int. J. Electrochem. Sci.*, 9 **(2014)** 3951 - 3960

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

# Inhibitive Effects by Some Benzothiazole Derivatives on Mild Steel Corrosion in 1 N HCl

*N. S. Patel*[*], *P. Beranek, M. Nebyla, M. Přibyl, D. Šnita*

Department of Chemical Engineering, Institute of Chemical Technology, Technická 5, Prague 6, Czech Republic.
[*]E-mail: niketan.ptl@gmail.com

*Received:* 14 February 2014 / *Accepted:* 21 March 2014 / *Published:* 14 April 2014

The inhibition effect of some Benzothiazole derivatives 1,3-benzothiazol-2-amine (BTA), 6-methyl-1,3-benzothiazol-2-amine (MBTA) and 2-amino-1,3-benzthiazole-6-thiol (TBTA) against mild steel corrosion in 1 N HCl solutions were evaluated using conventional weight loss, potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy. The weight loss results showed that all the three organic compounds are excellent corrosion inhibitors, electrochemical polarizations data discovered the mixed mode of inhibition and the results of electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the inhibitors employed is due to the adsorption of the molecule leading to the formation of a protective layer on the surface of mild steel. The inhibition efficiencies increased with increase in concentration followed the order of TBTA > MBTA > BTA.

**Keywords:** Benzothiazole derivatives; corrosion inhibition; electrochemical polarization; electrochemical impedance spectroscopy; mild steel.

## 1. INTRODUCTION

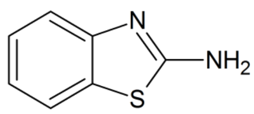
The corrosion of iron and mild steel (MS) is a fundamental academic and industrial concern that has received a considerable amount of attention [1, 2]. In addition; they are exposed to various corrosive environments including acids, alkalis and salts. Out of this, hydrochloric acid is one of the most commonly used chemical for industries for removal of the undesired scales and rust. The addition of corrosion inhibitors are believed to be one of the best methods in this environments as they secures the metal against these severe acid attacks. Inhibitors are generally used in these processes to control metal dissolution [3] and, during past decade many organic inhibitors have been studied in different media [4-9]. The mechanism of their action can be different, depending on the metal, the medium and the structure of the inhibitor. One possible mechanism is the adsorption of the inhibitor, which blocks the metal surface and thus do not permit the corrosion process to take place. Many N-heterocyclic compounds with polar groups and/or π-electrons are efficient inhibitors of the corrosion of steel and iron in acidic media [10-13]. This kind of organic molecules can adsorb on the metal surface because it can form a bond between the N electron pair and/or the π-electron cloud and the metal thereby reducing the corrosive attack on metals in acidic media [10].

The present work is aimed at the use of some benzothiazole derivatives 1,3-benzothiazol-2-amine (BTA), 6-methyl-1,3-benzothiazol-2-amine (MBTA) and 2-amino-1,3-benzthiazole-6-thiol (TBTA) against mild steel corrosion in 1 N HCl solutions. The electrochemical behavior of MS in HCl media in the absence and presence of above three inhibitors has been studied by weight loss method, potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy (EIS).

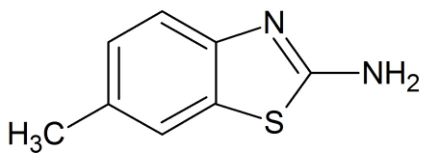
## 2. EXPERIMENTAL

### *2.1. Inhibitor Preparation*

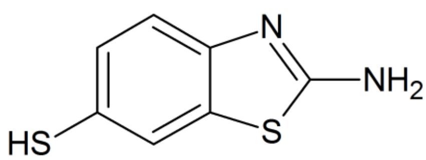
The benzothiazole derivatives were synthesized according to previously reported an experimental procedure [14, 15]. The molecular formulas of benzothiazole derivatives are shown in Fig. 1.The choice of the compounds are based on molecular structure considerations; the presence of nitrogen, sulfur atoms and aromatic rings is likely to facilitate the adsorption of the compound on the metal surface.




1, 3-benzothiazol-2-amine (BTA) {Molar mass: 150.20 g/mol}




6-methyl-1, 3-benzothiazol-2-amine (MBTA) {Molar mass: 164.23 g/mol}




2-amino-1, 3-benzthiazole-6-thiol (TBTA) {Molar mass: 182.27 g/mol}

**Figure1.** Molecular structures of benzothiazole derivatives

### *2.2. Preparation of Electrodes*

As described above three types of electrodes were used in the study. To prepare WE, mild steel (MS) rod sample **(**0.09% P, 0.37% Si, 0.01% Al, 0.05% Mn, 0.19% C, 0.06% S and the remainder Fe**)** was obtained and carefully cut into many cylindrical electrodes. The upper area of the WE was then precisely covered with the Teflon and epoxy coating. The area of exposed surface of WE was measured precisely, with Vernier caliper. For the weight loss method specimens used (length = 2 cm, width = 2 cm, thickness = 0.1 cm) with a tiny hole on the upper part of it. This prepared WE was washed with a luke warm mild detergent (Surf) solution to remove greasy materials and then cleaned and washed repeatedly with double distilled water. It was quickly dried with a soft tissue paper and air dried then shifted into a desiccator or into the electrolyte in polarization cell.

### *2.3. Weight Loss Method*

The polished and pre-weighed MS specimens were tied with threads and suspended in 100 ml test solutions, 1.0 M $H_2SO_4$ with and without the inhibitor of different concentrations, for 2 h of immersion. After the immersion test, the specimens were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each set of the test and the mean value of the weight loss (WL) is reported. The loss in weight was determined by analytic digital micro-balance.

### *2.4. Electrochemical and Impedance Measurements*

The electrochemical polarizations were carried out in a three neck polarization cell. Platinum gauze and saturated calomel electrode (SCE) were employed as counter and reference electrode, respectively. The surface area of 1 $cm^2$ of WE was exposed to the electrolyte solution of 1 M H2SO4 and various concentration of plant extracts. The electrochemical impedance spectroscopy (EIS) measurements are obtained as Nyquist plots and electrochemical polarization data's as Tafel plots. The Electrochemical Analyser Workstation (Autolab – PGSTAT 302N) was used for measuring data's. Polarization curves were attained with a scan rate of 0.01 V/s in the range of ± 10 mV for linear polarization resistance (LPR) and ± 250 mV for Tafel plots vs. the $E_{corr}$ of the WE and measured against the SCE.

## 3. RESULTS AND DISCUSSION

### *3.1. Weight Loss Measurements*

Based on the weight loss measurements, the corrosion rates ($W_{corr}$) and the values of inhibition efficiency ($E_w$%) for various concentrations of BTA, MBTA and TBTA after 2 h of immersion of the

MS coupons in 1 N HCl, obtained are given in Table - 1. The values of $E_w$% were calculated by the following equation.

$$E_W\% = 100 \times \frac{W_0 - W_{corr}}{W_0} \quad (1)$$

Where $W_{corr}$ and $W_0$ are the corrosion rates of MS with and without the additive, respectively.

**Table 1.** Inhibition Efficiency of MS in 1 N HCl in presence and absence of different concentrations of BTA, MBTA and TBTA (constructed on the basis of Weight loss method)

| Inhibitor | Concentration of inhibitor (ppm) | W ($\mu$g/cm$^2$ h) | Inhibition Efficiency $E_W$% |
|---|---|---|---|
| | 0 | 18.45 | - |
| BTA | 10 | 9.34 | 49.38 |
| | 20 | 8.74 | 52.63 |
| | 30 | 7.65 | 58.54 |
| | 40 | 6.68 | 63.79 |
| | 50 | 6.01 | 67.42 |
| MBTA | 10 | 8.08 | 56.21 |
| | 20 | 7.35 | 60.16 |
| | 30 | 6.21 | 66.34 |
| | 40 | 5.75 | 68.83 |
| | 50 | 5.14 | 72.14 |
| TBTA | 10 | 7.16 | 61.19 |
| | 20 | 6.36 | 65.53 |
| | 30 | 5.51 | 70.14 |
| | 40 | 4.95 | 73.17 |
| | 50 | 4.36 | 76.37 |

From the above table, it is observed that the value of $E_w$% increases with the increase in the concentration of the inhibitor, suggesting that the number of molecules adsorbed of the three additives were increased over the MS surface, blocked the active sites of acid attack and thereby protecting the metal from accelerated corrosion attack.

This is also confirmed by Fig. 2. Out of which, TBTA achieved a maximum value of 76.37% inhibition efficiency at the highest concentration of 50 ppm employed. And according to the WL measurements the IE % obtained, followed the trend TBTA > MBTA > BTA.

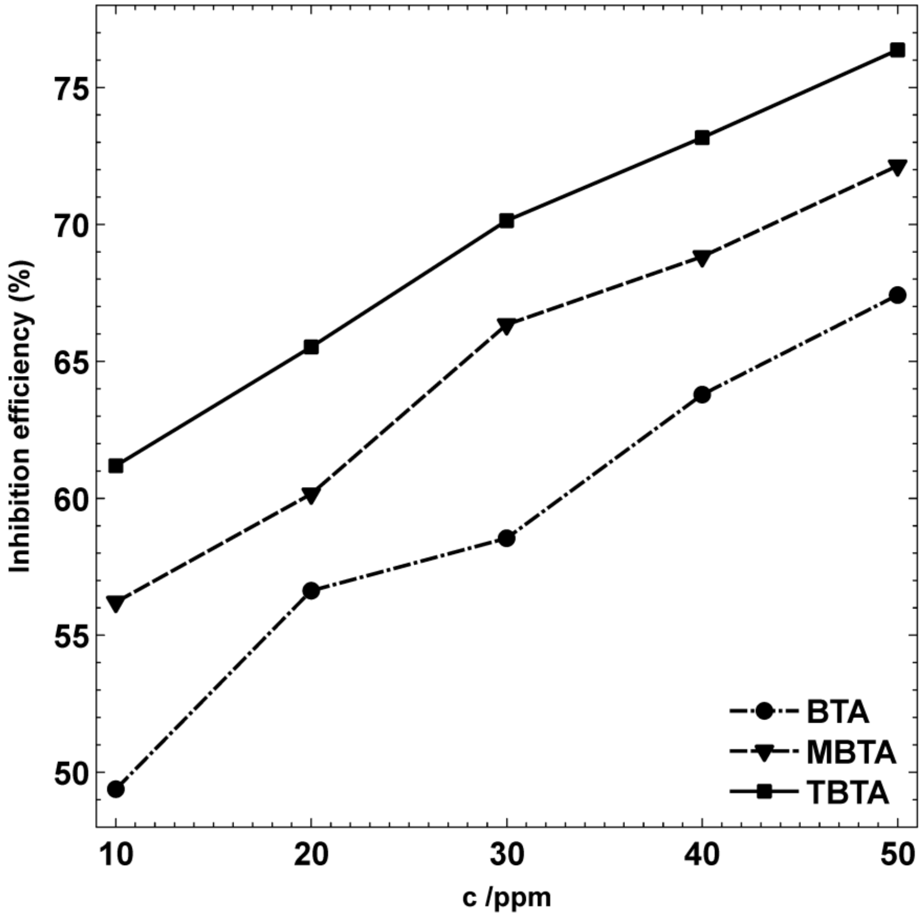



**Figure 2.** Inhibition efficiencies against the various concentrations of the additives studied using WL method

*3.2. Electrochemical polarizations*

The potentiodynamic polarization data's are shown in Fig. 3 as the representative Tafel plots for MS in 1 N HCl solutions with the addition of various concentrations of all the three additives. The values of $E_I$ % were calculated using the following equation.

$$E_I\% = 100 \times \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \qquad (2)$$

where $I_{corr}$ and $I_{corr(inh)}$ are the values of corrosion current densities of MS without and with the additive, respectively.

The inhibiting properties of the tested BTA, MBTA and TBTA have also been evaluated by the determination of the polarisation resistance. The corresponding polarisation resistance ($R_p$) values of MS in 1 N HCl in the absence of different concentrations of the additives are given in Table-2. The inhibition efficiency ($E_{Rp}$%) was defined as follows:

$$E_{Rp}\% = 100 \times \frac{R_{P(inh)} - R_P}{R_{P(inh)}} \qquad (3)$$

$R_p$ and $R_{p(inh)}$ are the polarisation resistance in the absence and in the presence of the inhibitor, respectively.

From the Table-2, it is observed that in all the three cases of BTA, MBTA and TBTA the corresponding corrosion current density of MS in inhibited solutions are much lower than in the uninhibited solutions. Furthermore, there was an anodic shift of the $E_{corr}$ value with the increase in the concentration of the inhibitors signifying that BTA, MBTA and TBTA have acted as anodic inhibitors [16-20] for MS in 1 N HCl which was supported by the slow and study decrease of anodic Tafel slope values. From these decrease it could be said that the rate of anodic dissolution was much retarded in comparison to that of cathodic hydrogen evolution. There was also slight decrease in the corresponding values of cathodic Tafel slopes too. This means that BTA, MBTA and TBTA must have acted predominantly by blocking anodic sites and also cathodic sites to some extent, so they behaved as mixed-type of the acid corrosion inhibitors. When compared to the above mentioned reference papers the studied compound behaved similarly as previously reported benzimidazole derivatives. And the mechanism step might follow the similar route as the anodic reaction of MS corrosion in strong acidic media causes the formation of ferrous species. The N atoms of benzimidazole derivatives with unshared electron pair can coordinate with the Fe (II) species to form insoluble Fe (II)-inhibitor complex. The complex may deposit onto the active sites to inhibit the dissolution of iron.

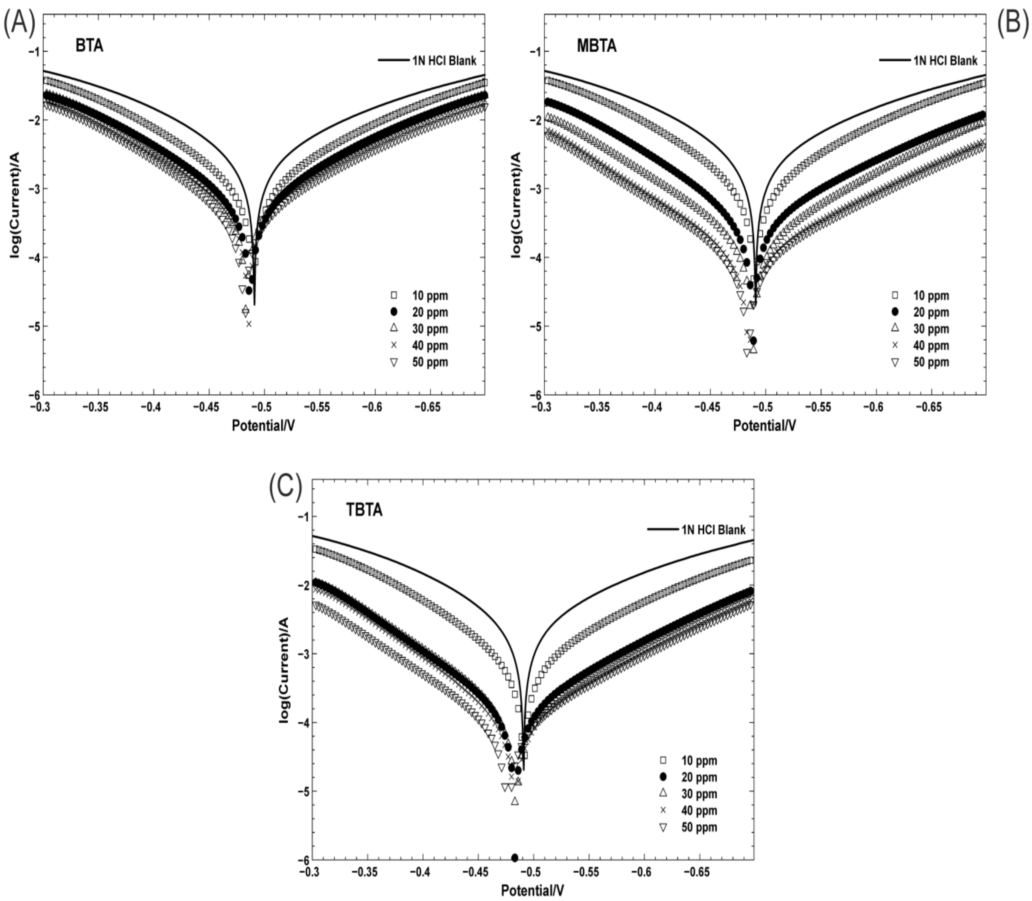



**Figure 3.** Tafel plots showing effect of BTA, MBTA and TBTA on corrosion of MS in HCl medium

**Table 2.** Effect of BTA, MBTA and TBTA on MS in 1 N HCl media (Electrochemical polarization studies)

| Inhibitor | Concentration of inhibitor (ppm) | $E_{corr}$ V | Tafel Constant (mV/decade) ba | bc | $I_{corr}$ ($mA/cm^2$) | $R_p$ (ohm $cm^2$) | $E_I$ % | $E_{Rp}$% |
|---|---|---|---|---|---|---|---|---|
| BTA | 0 | -0.4909 | 129 | 144 | 3.004 | 10 | - | - |
| | 10 | -0.4897 | 103 | 118 | 1.114 | 20 | 62.9 | 50 |
| | 20 | -0.4871 | 101 | 116 | 0.632 | 39 | 79 | 74.4 |
| | 30 | -0.4840 | 96 | 115 | 0.540 | 43 | 82 | 76.7 |
| | 40 | -0.4829 | 97 | 116 | 0.497 | 51 | 83.5 | 80.4 |
| | 50 | -0.4816 | 96 | 115 | 0.383 | 63 | 87.3 | 84.1 |
| MBTA | 0 | -0.4909 | 129 | 144 | 3.004 | 10 | - | - |
| | 10 | -0.4901 | 101 | 120 | 1.062 | 25 | 64.6 | 60 |
| | 20 | -0.4895 | 95 | 118 | 0.315 | 71 | 89.5 | 85.9 |
| | 30 | -0.4879 | 95 | 117 | 0.162 | 118 | 94.6 | 91.5 |
| | 40 | -0.4842 | 94 | 118 | 0.106 | 211 | 96.5 | 95.3 |
| | 50 | -0.4831 | 96 | 119 | 0.090 | 248 | 97 | 96 |
| TBTA | 0 | -0.4909 | 129 | 144 | 3.004 | 10 | - | - |
| | 10 | -0.4904 | 98 | 119 | 0.698 | 33 | 76.8 | 69.7 |
| | 20 | -0.4836 | 87 | 112 | 0.147 | 139 | 95.1 | 92.8 |
| | 30 | -0.4831 | 87 | 111 | 0.138 | 151 | 95.4 | 93.4 |
| | 40 | -0.4825 | 86 | 111 | 0.101 | 215 | 96.6 | 95.3 |
| | 50 | -0.4762 | 86 | 109 | 0.079 | 260 | 97.4 | 96.2 |

The $R_p$ values of MS in 1 N HCl in the absence and presence of different concentrations of the tested inhibitors are also given in Table-2. From the results, $R_p$ values gradually increased with increase in the concentration of inhibitors. The values of inhibition efficiency of BTA, MBTA and TBTA obtained by electrochemical polarizations are in good agreement. And according to the $I_{corr}$ and $R_p$ values the IE % obtained, followed the trend TBTA > MBTA > BTA.

*3.3. Electrochemical impedance spectroscopy*

The corrosion behavior of MS in 1 N HCl, in absence and the presence of various concentrations of BTA, MBTA and TBTA were also investigated by EIS technique. The resultant Nyquist plots are shown in Fig. 4. The values of inhibition efficiency ($E_R$ %) were calculated by the equation as follows.

$$E_R\% = 100 \times \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \qquad (4)$$

Where $R_t$ and $R_{t(inh)}$ are the charge-transfer resistance values in absence and the presence of the additives, respectively.

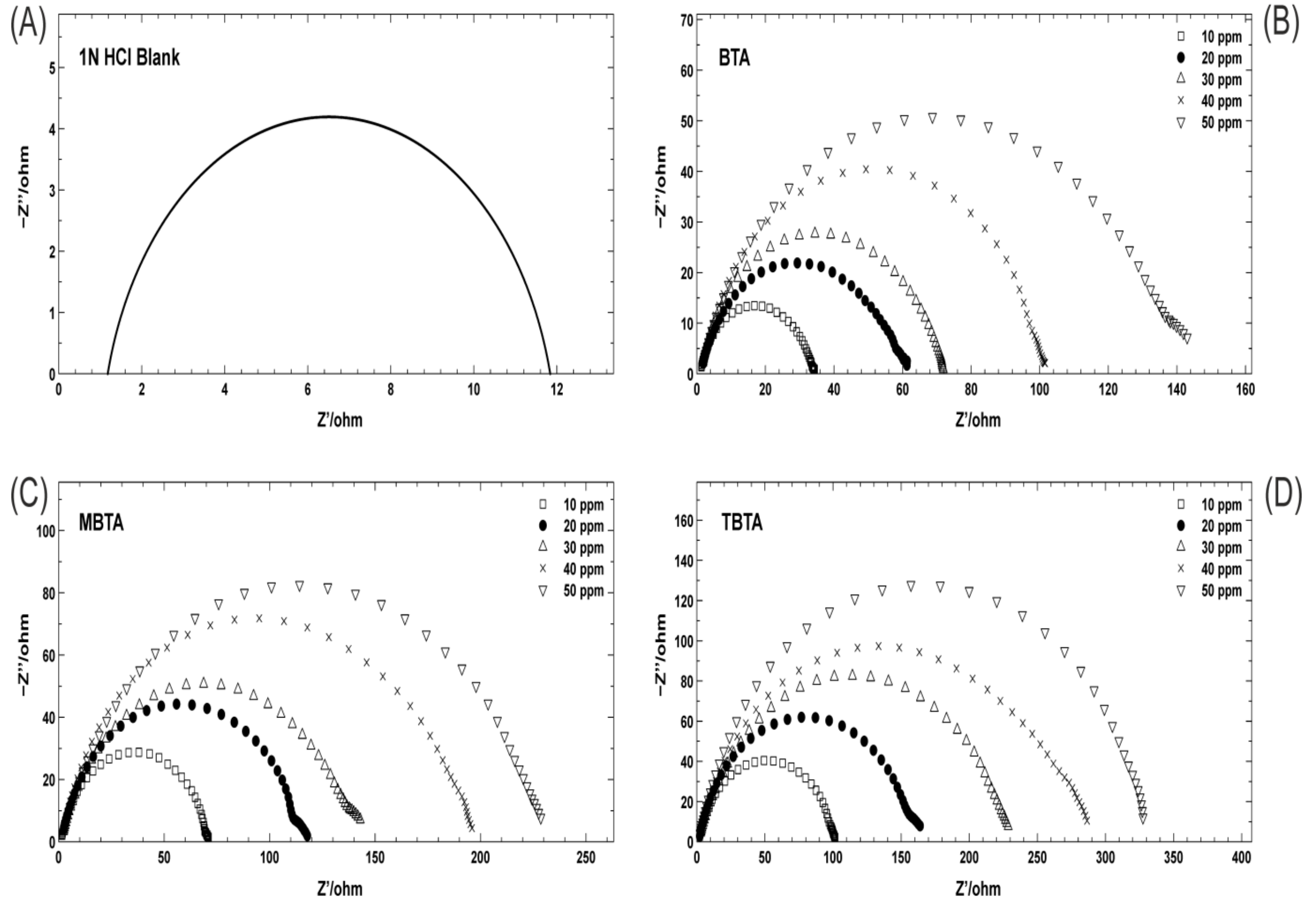



**Figure 4.** Nyquist plots showing effect of A) 1 N HCl, B) BTA, C) MBTA and D) TBTA on corrosion of MS in HCl medium

To obtain the values of double layer capacitance ($C_{dl}$), the values of frequency at which the imaginary component of the impedance is maximum $-Z_{im(max)}$ was found and used in the following equation with corresponding $R_t$ values:

$$C_{dl} = \frac{1}{2\pi f_{\max} R_t} \quad (5)$$

The existence of a single semicircle in Nyquist plot shows that there was only single charge transfer process during the anodic dissolution of MS and remained unaffected in the presence of BTA, MBTA and TBTA added in the acid solutions. An isolated Nyquist plot for the blank system is shown in Fig. 4A and the value of real impedance (Z') was only 11 Ohms which indicated that there was least charge transfer resistance ($R_t$) of the corrosion reactions. There was regular rise in the diameter of each semicircle of the Nyquist plots when the concentration was raised from 10 to 50 ppm for all the three additives. This increase of the diameters clearly reflected that the $R_t$ values also increased at highest concentration of 50 ppm due to formation and gradual improvement of the barrier layer of the inhibitive molecules, and as a result the acid corrosion rate of MS gradually decreased.

**Table 3.** Data from electrochemical impedance measurements of mild steel in 1 N HCl for various concentrations of BTA, MBTA and TBTA

| Inhibitor | Concentration of inhibitor (ppm) | $R_t$ Ohm.cm$^2$ | Cdl µF/cm$^2$ | Inhibition Efficiency $E_R$(%) |
|---|---|---|---|---|
| BTA | 0 | 11 | 148.22 | - |
| | 10 | 33 | 133.76 | 66.7 |
| | 20 | 60 | 126.53 | 81.7 |
| | 30 | 73 | 112.96 | 84.9 |
| | 40 | 102 | 101.31 | 89.2 |
| | 50 | 141 | 87.34 | 92.2 |
| MBTA | 0 | 11 | 148.22 | - |
| | 10 | 71 | 98.78 | 84.5 |
| | 20 | 114 | 93.27 | 90.4 |
| | 30 | 139 | 87.31 | 92.1 |
| | 40 | 198 | 82.48 | 94.4 |
| | 50 | 232 | 80.18 | 95.3 |
| TBTA | 0 | 11 | 148.22 | - |
| | 10 | 102 | 90.65 | 89.2 |
| | 20 | 165 | 89.24 | 93.3 |
| | 30 | 227 | 84.89 | 95.2 |
| | 40 | 287 | 81.36 | 96.2 |
| | 50 | 329 | 78.68 | 96.7 |

Table-3 embodies various parameters such as $R_t$ and $C_{dl}$. There was a gradual decrease in values of $C_{dl}$ with increase in the concentration of BTA, MBTA and TBTA. The double layer between the charged metal surface and the solution is considered as an electrical capacitor [21, 22]. And according to this phenomenon, the adsorption of the BTA, MBTA and TBTA on the electrode decreases its electrical capacity because they displace the water molecule and others ions originally adsorbed on the surface. The decrease of this capacity with increasing BTA, MBTA and TBTA concentrations may be associated with the formation of a protective layer at electrode surface. Inhibition efficiency is found to increase with BTA, MBTA and TBTA concentration. And the results obtained from EIS show the similar trend as those obtained from electrochemical polarisations and weight loss measurements.

Analysis of the electrochemical data show that the inhibiting properties increase with inhibitor concentration. The inhibition efficiency increases in accordance to the order: TBTA > MBTA > BTA for all concentrations. It is not surprising that TBTA, which possess additional heteroatoms with lone pairs for adsorption to the MS surface, is better inhibitor than MBTA and BTA. But it must be noticed that both MBTA and BTA too worked well enough to become potential inhibitors for MS in HCl medium.

## 4. CONCLUSIONS

The protection effectiveness with the addition of all the three inhibitors increases with the increase of the inhibitor concentration. In addition, for all the methods studied IE % obtained, followed the trend TBTA > MBTA > BTA. Polarization measurements have shown that they all have acted as mixed type corrosion inhibitors, retarding mainly anodic dissolution of steel in 1 N HCl. The results of the weight loss, electrochemical polarizations and EIS were all in very good agreement to support the above conclusions. And these three benzothiazole derivatives possessed all the characteristics which the industries require for potential inhibitor applications.

ACKNOWLEDGEMENT
The authors are grateful for support from the Technological Agency of the Czech Republic (Grant No. TA01010353).

## References

1. G. Avci, *Colloids Surf. A* 317 (2008) 730
2. F. Bentiss, F. Gassama, D. Barbry, L. Gengembre, H. Vezin, M. Lagrenee and M. Traisnel, *App. Surf. Sci.* 252 (2006) 2684
3. F. Bentiss, M. Traisnel and M. Lagrenée, *Corros. Sci.* 42 (2000) 127
4. N. S. Patel, S. Jauhari and G. N. Mehta, *Acta Chim. Slov.* 57 (2010) 297
5. N. S. Patel, S. Jauhari, G. N. Mehta, B Hammouti, S S Al-Deyab and M. Bouachrine, *J. Iran Chem. Soc.* 9 (2012) 635
6. R. A. Prabhu, A. V. Shanbhag and T. V. Venkatesha, *J. Appl. Electrochem.* 37 (2007) 491
7. N. S. Patel, S. Jauhari and G. N. Mehta, *Chem. Pap.* 64 (1) (2010) 51
8. H. Vashisht, S. Kumar, I. Bahadur and G. Singh, *Int. J. Electrochem. Sci.* 8 (2013) 684
9. S. K. Shukla, A. K. Singh and M. A. Quraishi, *Int. J. Electrochem. Sci.* 7 (2012) 3371
10. Riggs Jr., O.L. (1973). Theoretical Aspects of Corrosion Inhibitors and Inhibition. in: C.C. Nathan (Ed.), *Corrosion Inhibitors*, Houston, TX, USA
11. G. Schmitt, *Br. Corros. J.* 19 (1984) 165-176
12. K. Tebbji, I. Bouabdellah, A. Aouniti, B. Hammouti, H. Oudda, M. Benkaddour and A. Ramdani, *Mater. Lett.* 61 (2007) 799
13. G. Trabanelli, *Corrosion* 47 (1991) 410
14. M. Wang, M. Gao, B. H. Mock, K. D. Miller, G. D. Hutchinsa and Q. H. Zhenga, *Bioorg. Med. Chem.* 14 (2006) 8599
15. A. Rana, N. Siddiqui, S. A. Khan, S. E. Haque and M. A. Bhat, *Eur. J. Med. Chem.* 43 (2008) 1114
16. H. H. Uhlig and R.W. Revie, *Corrosion and Corrosion Control*, Wiley, New York (1985)
17. Y. Yan,W. Li, L. Cai and B. Hou, *Electrochim. Acta*, 53 (2008) 5953
18. J. Aljourani, K. Raeissi and M. A. Golozar, *Corros. Sci.* 51 (2009) 1836
19. Y. Tang, F. Zhang, S. Huc, Z.Cao, Z. Wua and W. Jing, *Corros. Sci.*74 (2013) 271
20. J. Aljourani, M. A. Golozar and K. Raeissi, *Mater.Chem. Phy.* 121 (2010) 320
21. O.L. Riggs Jr., in: C.C. Nathan (Ed.), *Corrosion Inhibitors*, Houston, TX, USA (1973)
22. F. Bentiss, M. Lagrenée, M. Traisnel and J.C.Hornez, *Corros. Sci.* 41 (1999) 789

© 2014 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).