# Benzothiazole Derivatives as Corrosion Inhibitors for Carbon Steel in 1 M H<sub>3</sub>PO<sub>4</sub> Solutions

A.S. Fouda<sup>a\*</sup>, M. Diab<sup>b</sup>, A. El-Sonbaty<sup>b</sup>, Sh.A. Hassan<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura, 35516, Egypt <sup>b</sup> Department of Chemistry, Faculty of Science, Damietta University, New Damietta, 34517, Egypt

\*Corresponding author (Tel: +20.50.2365730; Fax: +20.50.2246254, email: asfouda@mans.edu.eg)

#### Abstract

The inhibition of the corrosion of carbon steel in 1 M  $H_3PO_4$  solutions by some benzothiazole derivatives has been investigated using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Inhibition was found to increase with increasing concentration of the benzothiazole derivatives but decreased with rise in temperature. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of these compounds on carbon steel surface obeys the Temkin's adsorption isotherm. Potentiodynamic polarization measurements showed that benzothiazole derivatives act as mixed-type inhibitors.

Keywords: Carbon steel, corrosion inhibition, benzothiazole derivatives, phosphoric acid, quantum chemical calculations

# Introduction

Phosphoric acid  $(H_3PO_4)$  is a medium-strong acid, but it still shows strong corrosiveness on ferrous alloy [1]. H<sub>3</sub>PO<sub>4</sub> is widely used in surface treatment of steel such as chemical and electrolytic polishing, chemical coloring. chemical and electrolytic etching, removal of oxide film, phosphating, passivating, and surface cleaning. Little work appears to have been done on the inhibition of carbon steel in H<sub>3</sub>PO<sub>4</sub> solution. Using inhibitors is an effective method for corrosion to control the corrosion of metals. Inhibitors are compounds that control corrosion processes of metals. Many studies on inhibitors have been carried out [2-24], among them nitrogen containing inhibitor is one of the focuses of the studies [8-24]. Bentiss et al. [11], El Azhar et al. [16] and Elkadi et al. [20] have investigated many nitrogen-containing inhibitors for the corrosion inhibition of steel in HCl and H<sub>2</sub>SO<sub>4</sub>, their studies show that nitrogen-containing organic inhibitor acts as a strong inhibitor for steel in HCl, compared with H<sub>2</sub>SO<sub>4</sub>. Triazole and triazole-type compounds containing nitrogen, sulphur and heterocycle on the corrosion inhibition of metal in acidic media have attracted more attention because of their excellent corrosion inhibition performance [25-28]. The researches by Fouda et al. [48] showed that some 4-phenylthiazole derivatives could inhibit the corrosion of 304 L stainless steel in hydrochloric acid solution, but the inhibition effect was not very excellent [29]. However, synergistic effect occurred on addition of KSCN to acid containing 4-phenylthiazole derivatives which inhibited 304 L stainless steel corrosion, and the phenomenon synergism took place at very low of

concentrations for the systems studied. Wang et al. [30] also investigated the effect of some mercapto-triazole derivatives synthesized containing different hetero atoms and substituents in the organic structures on the corrosion and hvdrogen permeation of mild steel in hydrochloric acid solution and their results revealed that all the mercapto-triazole derivatives performed excellently as corrosion inhibitors[30]. Especially, some N-and S-containing triazole derivatives environmentally are friendly corrosion inhibitors compared with some commercial acid corrosion inhibitors which are highly toxic, such as chromate and nitrite [31]. Little work appears to have been done on the inhibition of carbon steel in H<sub>3</sub>PO<sub>4</sub> solution. In this work, benzothiazole derivatives containing nitrogen, sulphur and aromatic ring had been studied on the corrosion inhibition of carbon steel  $H_3PO_4$ solutions weight in by loss. potentiodynamic polarization, electrochemical spectroscopy impedance (EIS) and electrochemical frequency modulation (EFM) techniques.

#### Materials and methods

# Materials preparation

The chemical composition wt % of carbon steel was as follows: 0.200 C, 0.350 Mn, 0.024 P, 0.003 Si, 0.023 and the remainder Fe. Seven pieces of carbon steel were cut into 2 x 2 x 0.2 cm .The specimens were polished with a series of emery papers of different grit size up to 1200, degreased in acetone [32], rinsed with double distilled water and finally dried between two filter papers and then weighed. After that these specimens were immersed in 100 ml solution of H<sub>3</sub>PO<sub>4</sub> without and with different concentrations of the studied inhibitors for 3 hours at temperature range from 25°C to 55° C, at the end of the tests the specimens were taken out, washed, dried and weighed again. Then the average weight loss calculated at certain time of each specimen was taken.

# Electrochemical techniques

For Electrochemical measurements (potentiodynamic polarization, EIS and EFM techniques) the cell used was a conventional three electrodes Pyrex glass with a platinum foil counter electrode and standard calomel electrode (SCE) as reference. The working electrode was carbon steel electrode, which cut from carbon steel sheets with thickness 0.1 cm. The electrode was of dimensions 1 cm x 1 cm and was weld from one side to a copper wire used for electric connection. The sample was embedded in a glass tube using epoxy resin [33]. The cell was filled with constant quantity of the test solution (100 ml). The electrode potential was allowed to stabilize for 30 min before starting the measurements. The potentiodynamic currentpotential curves were recorded by changing the electrode potential automatically from - 500 to + 500 mV with a scan rate of 5 mV s<sup>-1</sup>. Experiments for electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range of 100 kHz to 10 mHz at open circuit potential (OCP). The amplitude was 5 mV. Experiments for electrochemical frequency modulation (EFM) measurements were carried out using two frequencies 2 and 5 Hz. The base frequency was 1Hz with 32 cycles, so the waveform repeats after 1s. A perturbation signal with amplitude of 10 mV was used. The choice for the frequencies of 2 and 5 Hz was based on three principles [34]. The electro-chemical measurements were carried out using Potentiostat/Galvanostat/Zera analyzer (Gamry PCI 300/4). This includes Gamry framework system based on the ESA400, and a personal computer with DC 105 software for potentiodynamic polarization, EIS 300 software for EIS and EFM 140 software for EFM measurements. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

# Inhibitors

Table 1 shows the molecular structure, names, molecular formula and molecular weight of the investigated compounds, which has been labeled and C. The synthesis by A. B and characterization (spectral measurements) of the PAMT was as described and documented Appropriate elsewhere previously [35]. concentration of acid (H<sub>3</sub>PO<sub>4</sub>) was prepared by diluting by double-distilled water.

# **Results and Discussion**

### Weight loss measurements

Weight loss of carbon steel was determined at several time intervals in the absence and presence

of different concentrations of benzothiazole derivatives (A-C). Fig. 1 shows the weight losstime curves for carbon steel corrosion at different concentrations of inhibitor (A), the most effective one at 25°C. Similar curves were obtained for other compounds (not shown). The curves obtained show that the weight loss of carbon steel in presence of inhibitor is lower than free acid decreases with increasing inhibitors and concentrations [36]. This means that these compounds act as inhibitors for carbon steel in H<sub>3</sub>PO<sub>4</sub> solutions. The degree of surface coverage ( $\theta$ ) and the inhibition efficiency (%  $\eta$ ) were calculated using the following equation:

 $\%\eta = \theta x 100 = [1 - (W_{inh}/W_{free})] x 100$  (1)

where  $W_{inh}$  and  $W_{free}$  are the weight losses per unit area in presence and absence of the inhibitor, respectively. Values of %  $\eta$  are listed in Table 2. The values of inhibition efficiency increased with increasing inhibitor concentration. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of inhibitors with the increase of its concentration. At the same concentration of inhibitors, the order of inhibition efficiency was found to be as follows: A> B > C.

Table 1 The chemical structure of the investigated benzothiazole derivativ
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Comp	Structure	Names & molecular formula	molecular weight
(A)	H <sub>2</sub> N CH <sub>3</sub>	5-amino-4(Benzo[d]thiazole-2- yl)-1-p-toly1-1H-pyrrol-3-ol	321.4
(B)	H <sub>2</sub> N H <sub>2</sub> N CI	5-amino-4(Benzo[d]thiazole-2- yl)-1-(4Chlorophenyl)-1H-pyrrol- 3-ol	341.8
(C)	H <sub>2</sub> N NO <sub>2</sub> N NO <sub>2</sub>	5-amino-4(Benzo[d]thiazole-2- yl)-1-(2Bromo-4,6Nitrophenyl)- 1H-pyrrol-3-ol	476.0

Table 2 Inhibition efficiency (% $\eta$ ) at different concentrations of inhibitors for the corrosion of carbon steel after 120 min immersion in 1 M H<sub>3</sub>PO<sub>4</sub> at 25 °C

Conc.,	(A)	(B)	(C)
μΜ	%η	%η	%η
1	48.3	32.7	26.1
5	50.8	51.6	34.9
10	70.6	58.0	50.0
15	72.7	62.2	58.4
20	77.3	68.1	63.4
25	81.1	70.6	65.1

#### Adsorption isotherm behavior

Benzothiazole derivatives inhibit corrosion of carbon steel by adsorbing onto the metal surface in acid solution. Basic information on the interaction between the inhibitor and the metal can be provided by the adsorption isotherm. The values of surface coverage ( $\theta$ ) corresponding to different concentrations of the inhibitor have been used to determine the adsorption isotherm. The variation of surface coverage ( $\theta$ ) determined

by weight loss with the logarithm of the inhibitor (A) concentration with log C, at different temperatures are represented in Fig. 2. Similar curves were obtained for other inhibitors (not shown). The linear relationships of  $\theta$  vs.log C depicted in Fig. 2 with correlation coefficient nearly equal to 1.0 (R<sup>2</sup> > 0.9) suggest that the adsorption of benzothiazole derivatives from 1 M H<sub>3</sub>PO<sub>4</sub> solution on carbon steel obeys the Temkin adsorption isotherm. According to this isotherm the surface coverage is related to inhibitor concentration by:

 $K_{ads}C = \exp(-2a\theta)$  (2)

where "a" is the molecular interaction parameter and  $K_{ads}$  is the equilibrium constant of the adsorption process. The free energy of adsorption  $\Delta G^{\circ}_{ads}$  was calculated from the following equation [36]:  $\Delta G^{\circ}_{ads} = - RT \ln (55.5 \text{ K})$  (3)

where 55.5 is the concentration of water in solution in mol  $l^{-1}$ , R is the universal gas constant and T is the absolute temperature. By applying the following the equation  $\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T \Delta S^{\circ}_{ads}$  and plot  $\Delta G^{\circ}_{ads}$  versus T linear relationships with slope equal (-  $\Delta S^{\circ}_{ads}$ ) and intercept of ( $\Delta H^{\circ}_{ads}$ ) were obtained. The data were collected in Table 3.

Table 3Thermodynamicparametersfortheadsorptionofbenzothiazolederivativesoncarbonsteelsurfacein 1M $H_3PO_4$  at different temperatures

Temp.	$K_{ads} x 10^{-6}$	$-\Delta G^{\circ}_{ads}$	$-\Delta H^{\circ}_{ads}$	$\Delta S^{\circ}_{ads}$
°C	$M^{-1}$	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	J mol <sup>-1</sup>
				$K^{-1}$
		(A)		
25	7.81	49.3		
35	7.06	50.7	21.1	95.3
45	4.96	51.4		
55	3.73	52.2		
		(B)		
25	3.56	47.3		
35	2.63	48.1	27.3	67.6
45	2.15	49.2		
55	1.25	49.3		
		(C)		
25	1.13	44.5		
35	0.72	44.8	27.4	56.9
45	0.54	45.5		
55	0.45	46.2		

From data in Table 3 we can conclude that:

• Negative sign of  $\Delta G^{\circ}_{ads}$  indicates that the adsorption of benzothiazole derivatives on carbon steel surface is proceeding spontaneously [37, 38].



**Fig. 1** Weight loss-time curves for the dissolution of carbon steel in the absence and presence of different concentrations of inhibitor (A) in 1 M  $H_3PO_4$  at 25°C



**Fig. 2** Temkin adsorption isotherm for carbon steel in 1 M  $H_3PO_4$  in the presence of different concentrations of inhibitor (A) at different temperatures

• Generally, values  $\Delta G^{\circ}_{ads}$  of up to -20 kJ mol<sup>-1</sup> are consistent with physisorption , while those around - 40 kJmol<sup>-1</sup> or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond . From the obtained values of  $\Delta G^{\circ}_{ads}$  it was found the existence of comprehensive adsorption (physisorption and chemisorption) [39], that is to say, since the adsorption heat approached the general chem.-ical reaction heat, the chemical adsorption occurs.

- Negative sign of  $\Delta H^{\circ}_{ads}$  indicates that the process of adsorption is exothermic [40].
- Positive sign of  $\Delta S^{\circ}_{ads}$  arises from substitutional process, which can be attributed to the increase in the solvent entropy. This lead to an increase in disorder due to the fact that more water molecules can desorbed from the metal surface by one inhibitor.

# Effect of temperature

The effect of temperature on both corrosion inhibition of carbon steel in 1 M H<sub>3</sub>PO<sub>4</sub> solution in the absence and presence of different concentrations of inhibitors at different temperatures ranging from 25 to 55 °C was investigated. The apparent activation energies  $(E_a^*)$  for the corrosion reaction of carbon steel in 1 M H<sub>3</sub>PO<sub>4</sub> solution in the absence and presence of different concentrations of benzothiazole derivatives calculated from Arrhenius were type equation [41]:

Log  $k_{corr} = \log A - E_a^* / (2.303 RT)$  (5)

where A is the Arrhenius pre-exponential factor. A plot of log  $k_{corr}$  versus 1/T gave straight lines as shown in Fig. 3. The enthalpy of activation ( $\Delta H^*$ ) and the entropy of activation ( $\Delta S^*$ ) were obtained by applying the transition-state equation [41]:

 $\log (k_{corr}/T) = [\log(R/Nh) + (A_{corr}/T)] = [\log$ 

 $(\Delta S^*/ 2.303R) - (\Delta H^*/ 2.303RT)](6)$ 



Electrochemical techniques

A plot of log ( $k_{corr}/T$ ) versus 1/T gave straight lines as shown in Fig. 4. With a slope of ( $-\Delta H^*/$ 2.303R) and intercept of [log(R/Nh) + ( $\Delta S^*/$ 2.303R)] from which the values of  $\Delta H^*$  and  $\Delta S^*$ were calculated, respectively. All estimated thermodynamic-kinetic parameters were tabulated in Table 4. The obtained data in Table 4 can be interpreted as follows:

- The presence of inhibitors increases the activation energies of carbon steel indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces energy barrier for the corrosion reaction and this barrier increases with increasing the inhibitor concentrations.
- Higher activation energy means lower reaction rate and the opposite is true. The increase in activation energy with inhibitor concentration is often interpreted by physical adsorption with the formation of an adsorptive film of an electrostatic character.
- Values of  $\Delta H^*$  are positive. This indicates that the corrosion process is an endothermic one.
- The entropy of activation  $(\Delta S^*)$  in the absence and presence of inhibitor has negative values, this indicates that the activated complex in the rate determining step represents an association rather than dissociation, meaning that, a decrease in disordering takes place on going from reactants to the activated complex[42].



**Fig. 3** Arrhenius plots for carbon steel dissolution in 1 M  $H_3PO_4$  in the absence and presence of different concentrations of inhibitor (A)

Fig. 4 Transition state plots for carbon steel dissolution in  $1 \text{ M H}_3\text{PO}_4$  in the absence and presence of different concentrations of inhibitor (A)

# Potentiodynamic polarization technique

The kinetics of anodic and cathodic reactions occurring on carbon steel electrodes in 1 M  $H_3PO_4$  in the absence and presence of different concentrations of benzothiazole derivatives was investigated using potentiodynamic polarization technique. Fig. 5 shows the polarization curves in the absence and presence of inhibitor (A) at 25 °C. Similar curves were obtained for other inhibitors (not shown). The numerical values of the variation of the corrosion current density ( $j_{corr}$ ), the corrosion potential ( $E_{corr}$ ), Tafel slopes ( $\beta_a \& \beta_c$ ), degree of surface coverage ( $\theta$ ) and the inhibition efficiency  $\eta_{Tafel}$  (%) were calculated from equation 7 & are given in Table 5.

 $\eta_{\text{Tafel}}\% = [1 - (j_{\text{corr}} / j_{\text{corr}})] \times 100$ 

where  $j_{corr}^{0}$  and  $j_{corr}$  correspond to uninhibited and inhibited corrosion current densities, respectively.

(7)



**Fig. 5** Polarization curves for the dissolution of carbon steel in 1 M  $H_3PO_4$  in the absence and presence of different concentrations of inhibitor (A) at 25 °C

The results indicate that:

1. The cathodic and anodic curves obtained exhibit Tafel–type behavior. Additional of benzothiazole derivatives increased both the anodic and cathodic overvoltages.

2. The corrosion current density  $(j_{corr})$  decreases with increasing the concentrations of the benzothiazole derivatives which indicates that these compounds acts as inhibitors, and the degree of inhibition depends on the concentrations of inhibitor. 3. The slopes of the anodic and cathodic Tafel lines ( $\beta_a \& \beta_c$ ) were slightly changed on increasing the concentrations of inhibitors. This indicates that there is no change of the mechanism of the inhibition in presence and absence of inhibitors .The benzothiazole derivatives are mixed-type inhibitors [43,44], but the cathode is more polarize than the anode when an external current was applied. The higher values of Tafel slopes can be attributed to surface kinetic process rather the diffusion-controlled process.

4. The order of inhibition efficiency of all inhibitors at different concentrations as given by polarization measurements are listed in Table 5. The results are in good agreement with that obtained from weight – loss measurements.

Table 4 Thermodynamic activation parameters for the dissolution of carbon steel in 1 M  $H_3PO_4$  in the absence and presence of different concentrations of investigated inhibitors

Inhibitor	H <sub>3</sub> PO <sub>4</sub> Conc. μM	A x 10 <sup>-9</sup> g cm <sup>-2</sup> min <sup>-1</sup>	${{{E_a}^*}\atop{kJ}} {mol^{-1}}$	$\Delta H^* \\ kJ \\ mol^{-1}$	$\begin{array}{c} -\Delta \text{ S}^{*} \\ \text{J} \\ \text{mol}^{-1} \\ \text{K}^{-1} \end{array}$
Blank	0.0	1.21	60.7	60.0	71.6
	1	2.06	62.6	64.7	66.9
	5	6.91	66.3	65.4	59.4
٨	10	25.40	70.3	66.4	58.4
А	15	41.40	71.8	67.0	57.4
	20	54.20	72.8	67.3	57.4
	25	370.00	78.1	69.5	51.1
	1	2.93	61.9	62.7	67.2
	5	3.96	64.0	63.4	66.0
D	10	17.80	68.6	64.0	65.4
D	15	17.50	69.1	65.4	61.5
	20	17.00	69.3	66.0	60.8
	25	24.30	70.5	67.8	56.5
	1	1.34	61.5	61.8	68.4
	5	2.35	63.0	62.3	67.9
C	10	8.79	66.4	63.4	65.8
C	15	7.20	66.8	65.1	61.6
	20	7.78	67.8	65.6	61.0
	25	12.4	68.7	66.4	60.2

# *Electrochemical impedance spectroscopy technique (EIS)*

Electrochemical impedance spectroscopy was used to characterized the corrosion inhibition and adsorbed behavior of carbon steel electrode in 1 M  $H_3PO_4$  containing various concentrations of benzothiazole derivatives. Fig. 6 the impedance diagrams consists of one large capacitive loop. In fact, the presence of inhibitors enhances the value of  $R_{ct}$  in acidic solution indicating a chargetransfer process mainly controlling the corrosion of carbon steel. The impedance parameters derived from this investigation are given in Table 6 these parameters can be concluded as follows:

•  $R_{ct}$  increased by increasing the concentrations of benzothiazole derivatives giving consequently a decrease in the corrosion rate.

•  $C_{dl}$  values decreased with increasing inhibitor concentration this is due to the gradual replacement of water molecules in the double layer by the adsorbed inhibitor molecules which form on adherent film on the metal surface and leads to decrease in the local dielectric constant of the metal solution interface [48].

•  $j_{corr}$  values decrease significantly in the presence of these additives and the %  $\eta$  is greatly improved. The order of reduction in  $j_{corr}$  exactly correlates with that obtained from potentiostatic polarization studies.

• The inhibition achieved by these inhibitors decreases in the following sequences A > B > C.

It can be concluded that the inhibition efficiency found from weight loss, polarization

curves and electrochemical impedance spectroscopy measurements are in good agreement.

Fig. 7 shows the typical EIS diagram obtained in 1 M  $H_3PO_4$  with and without inhibitor at frequency ranging from 100 kHz to 0.1 Hz.

The equivalent circuit model which describes the metal/electrolyte interface of the present corroding system is shown as insert in Fig. 8, where Rs, R<sub>ct</sub> and CPE refer to solution resistance, charge transfer resistance and constant phase element representing the double layer capacitance (C<sub>dl</sub>) of the interface, respectively. The charge transfer resistance (R<sub>ct</sub>) is calculated from the difference in impedance at lower and higher frequencies [45]. The double layer capacitance (C<sub>dl</sub>) and the frequency at which the imaginary component of impedance is maximal (-Z<sub>max</sub>) are found as the follow [46].

$$C_{dl} = 1 / (2 \pi \text{ fmax } R_{ct})$$
 (8)

The inhibition efficiencies obtained from the EIS measurements are calculated from the relation [47]:

% η =  $[1 - (R_{ct} / R_{ct})] x100$  (9)

where  $R_{ct}$  and  $R_{ct}^{}$  are the transfer resistance without and with the inhibitor, respectively.

Inh.	H <sub>3</sub> PO <sub>4</sub> C onc μM	-E <sub>corr,</sub> mV,vs SCE	j <sub>cor</sub> mA cm <sup>-2</sup>	$\beta_c$ mV dec <sup>-1</sup>	$mV_1^{\beta_a}$ dec	$\begin{array}{c} R_{P} \\ \Omega \ cm^{2} \end{array}$	θ	%η	CR mmy <sup>-1</sup>
Blank	0.0	524	5.527	767	648	27.60			64.152
	1	516	2.566	634	535	49.10	0.536	53.6	29.787
	5	486	2.413	608	489	48.80	0.563	56.3	28.505
^	10	480	1.087	471	393	85.60	0.836	83.6	10.512
A	15	482	0.645	432	361	132.50	0.883	88.3	7.489
	20	481	0.522	420	351	159.00	0.906	90.6	6.602
	25	476	0.318	362	309	229.50	0.942	94.2	3.695
	1	517	3.405	679	566	39.36	0.384	38.4	39.521
	5	499	2.505	613	497	47.62	0.546	54.6	29.075
D	10	477	1.027	477	391	90.38	0.814	81.4	11.918
D	15	477	0.737	446	369	119.00	0.867	86.7	8.552
	20	480	0.656	420	353	127.10	0.881	88.1	7.616
	25	482	0.470	408	343	172.10	0.915	91.5	5.452
	1	513	3.794	709	584	36.65	0.314	31.4	44.039
	5	516	3.437	677	561	38.76	0.378	37.8	39.899
G	10	504	2.602	639	522	47.92	0.529	52.9	30.202
C	15	507	1.799	559	471	61.69	0.675	67.5	16.342
	20	502	1.408	521	436	73.26	0.745	74.5	16.342
	25	500	1.165	481	406	82.05	0.789	78.9	13.522

Table 5 Electrochemical kinetic parameters obtained from potentiodynamic polarization technique for the corrosion of carbon steel in  $1 \text{ M H}_3\text{PO}_4$  at different concentrations of investigated inhibitors at 25 °C

**Table 6** Electrochemical kinetic parameters obtainedfrom EIS technique for the corrosion carbon steel in 1M  $H_3PO_4$  at different concentrations of investigatedinhibitors at 25° C

Inh	Conc µM	$C_{dl}x10^{-3},\ \mu F \text{ cm}^{-2}$	$R_{ct}$ , $\Omega cm^2$	θ	%η
blank	1 M H <sub>3</sub> PO <sub>4</sub>	124.0	12.81		
	1	60.0	33.65	0.619	61.9
•	5	46.8	42.84	0.701	70.1
A	10	44.8	45.72	0.720	72.0
	15	30.0	146.4	0.913	91.3
	1	55.7	29.13	0.560	56.0
р	5	49.1	32.43	0.605	60.5
D	10	56.6	35.41	0.638	63.8
	15	57.7	85.46	0.850	85.0
	1	96.1	27.06	0.527	52.7
C	5	82.2	28.76	0.555	55.5
C	10	50.9	31.27	0.590	59.0
	15	46.6	34.17	0.625	62.5

Electrochemical Frequency Modulation (EFM)

Several authors proposed electrochemical frequency modulation (EFM) as a new electrochemical technique for online corrosion monitoring [49-52]. EFM is a rapid and nondestructive corrosion rate measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants.



Fig. 6 Nyquist plots for carbon steel in 1 M  $H_3PO_4$  solution in the absence and presence of different concentrations of inhibitor (A) at 25 °C



Fig. 7 Electrical equivalent circuit used to fit the impedance data for carbon steel in 1 M  $H_3PO_4$  solution

In corrosion research, it is known that the corrosion process is non-linear in nature, a potential distortion by one or more sine waves will generate responses at more frequencies than the frequencies of applied signal. Virtually no attention has been given to the intermodulation or electrochemical frequency modulation. However, EFM showed that this non-linear response contains enough information about the corroding system so that the corrosion current can be calculated directly. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement. With the causality factors the experimental EFM data can be verified.

Fig. 9-12 show the current response contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies.

The larger peaks were used to calculate the corrosion current density  $(j_{corr})$ , the Tafel slopes ( $\beta_a$  and  $\beta_c$ ) and the causality factors (CF-2 and CF-3). These electrochemical corrosion kinetic parameters at different concentrations of inhibitors in 1 M H<sub>3</sub>PO<sub>4</sub> at 25 °C were simultaneously determined and are listed in Table 7. The inhibition efficiency %  $\eta$  calculated from Eq. (6), increases by increasing the studied inhibitor concentrations.

The causality factors CF-2 and CF-3 in Table 7 are close to their theoretical values of 2.0 and 3.0, respectively indicating that the measured data are of good quality. The calculated inhibition efficiency obtained from weight loss, Tafel polarization and EIS measurements are in good agreement with that obtained from EFM measurements.

# Mechanism of Corrosion Inhibition

The essential effect of these compounds as corrosion inhibitors is due to the presence of free

electron pairs in the nitrogen, oxygen and sulfur atoms, d  $\pi$ -electrons on the aromatic rings, molecular size, heat of hydrogenation, mode of interaction with the metal surface and formation of metallic complexes.

It is well known that carbon steel has coordination affinity toward N, O and S bearing ligand. Hence, adsorption on carbon steel can be attributed to co-ordination through hetero-atoms and  $\pi$ -electrons of aromatic rings [53]. In all investigated benzothiazole derivatives, there are unshared electron pairs on N, O and S, capable of forming  $\sigma$ -bond with carbon steel. Further, the double bonds in the molecule allow back donation of metal d-electron to the  $\pi^*$ -orbital.



Fig. 8 EFM spectra for carbon steel in 1 M H<sub>3</sub>PO<sub>4</sub> (blank)



Fig. 9 EFM spectra for carbon steel in 1 M  $H_3PO_4$  in the presence of  $1 \times 10^{-6}$  M from inhibitor (A)



**Fig. 10** EFM spectra for carbon steel in 1 M  $H_3PO_4$  in the presence of  $5 \times 10^{-6}$  M from inhibitor (A)



Fig. 11 EFM spectra for carbon steel in 1 M  $H_3PO_4$  in the presence of  $10x10^{-6}$  M from inhibitor (A)



Fig. 12 EFM spectra for carbon steel in 1 M  $H_3PO_4$  in the presence of  $15x10^{-6}$  M from inhibitor (A)

**Table 7** Electrochemical kinetic parameters obtained from EFM technique for carbon steel in 1 M  $H_3PO_4$  in the absence and presence of different concentrations of investigated inhibitors

Inhibitor	Conc., μM	$j_{corr.},$ $\mu A \text{ cm}^{-2}$	$\beta_a, mV dec^{-1}$	$\beta_c$ , mV dec <sup>-1</sup>	CF-2	CF-3	$\%~\eta_{EFM}$
blank	1 M H <sub>3</sub> PO <sub>4</sub>	948.6	155	293	1.981	3.054	
	1	788.4	135	259	1.993	2.441	16.9
•	5	586.8	191	191	1.977	3.284	38.1
A	10	263.2	129	130	1.945	2.747	72.3
	15	236.2	103	111	1.196	2.912	75.1
	1	797.6	151	220	1.979	2.894	15.9
р	5	697.4	138	207	1.976	2.238	26.5
D	10	590.8	136	203	1.961	3.290	37.7
	15	273.8	194	194	2.039	3.713	71.1
0	1	922.4	146	215	1.958	3.565	2.8
	5	809.6	149	217	1.949	2.736	14.7
C	10	796.3	145	211	1.959	3.495	16.0
	15	614.1	128	194	1.949	2.582	35.3

Another striking feature for high inhibition performance of all studied compounds is the presence of S-atom. The presence of S-atom in the inhibitor structure makes the formation of  $d\pi$  $d\pi$  bond resulting from overlap of 3d-electrons from carbon steel the 3d vacant orbital of S-atom possible, which enhances the adsorption of the compounds on the metal surface. Also the lower solubility of sulfur compounds and the greater polarizability of sulfur atoms increase the inhibition efficiency of these compounds.

The results show that among the investigated compounds inhibitor (A) exhibits the best performance because of the presence of highly electron releasing methyl group (with Hammett constant  $\sigma = -0.17$ ) [54]. The -CH<sub>3</sub> group increases the electron density on the active centers, which leads to great surface coverage, thereby giving higher inhibition efficiency. Compound (B) has the same number of active sites (S, N, O atoms) as compound (A) with replacement of methyl group by Cl atom. So, compound (B) comes next to compound (A) in the order of % inhibition and also, due to Cl atom act as electron withdrawing atom. Compound (C) is the least effective one; in spite of it has the same number of active sites (S, N, O atoms). This due to presence of two nitro groups (NO<sub>2</sub>) and one Br atom which all act as electron withdrawing groups. These groups will decrease the inhibition efficiencies.

# Conclusions

The investigated compounds show excellent performance as corrosion inhibitors in H<sub>3</sub>PO<sub>4</sub> solution. The inhibition efficiency of benzothiazole derivatives follows the order: A>B>C. Polarization studies showed that benzothiazole derivatives behave as mixed type inhibitors for carbon steel in H<sub>3</sub>PO<sub>4</sub> solution. Impedance studies indicated that R<sub>ct</sub> values increased, while C<sub>dl</sub> values decreased in the presence of the inhibitors. The adsorption of the investigated inhibitors was found to follow the Temkin adsorption isotherm indicating that the inhibition process occurs via adsorption. The  $\% \eta$ obtained from weight loss, polarization curves, electrochemical impedance spectroscopy and electrochemical frequency modulation are in good agreement

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الملخص العربي

# تثبيط تأكل الصلب الكربوني في محاليل من حمض الفوسفوريك باستخدام بعض مشتقات البنزوثيازول

عبد العزيز فودة<sup>1</sup>، مصطفى دياب<sup>2</sup>، عادل السنباطى<sup>2</sup>، شاهندة حسن<sup>2</sup> <sup>1</sup> قسم الكيمياء – كلية العلوم – جامعة المنصورة <sup>2</sup> قسم الكيمياء – كلية العلوم – جامعة دمياط

تم دراسة تثبيط تأكل الصلب الكربونى فى محلول 1 مولر حمض الفوسفوريك باستخدام بعض مشتقات البنزوثيازول باستخدام طريقة فقد الوزن، القياس البوتنشيوديناميكي، المعاوقة الكهربية، التركك الكهروكيمياائى. وجد أن تثبيط التأكل يزداد بزيادة تركيز مشتقات البنزوثيازول ولنه يقل برفع درجة الحرارة. وقد وجد أن الامتزاز الذي يتم علي سطح الصلب الكربوني يتبع ايزوثيرم. اثبت القياس البوتنشوديناميكي ان مشتقات البنزوثيازول تعمل آمثبطات من نوع مختلط.