

Full Length Research Paper

Benzothiazole derivatives as corrosion inhibitors for carbon steel in 1 M phosphoric acid (H₃PO₄) solutions

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Accepted 13 February, 2013

The inhibition of the corrosion of carbon steel in 1 M Phosphoric acid (H₃PO₄) solutions by some benzothiazole derivatives had 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 through 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.

Key words: Carbon steel, corrosion inhibition, benzothiazole derivatives, phosphoric acid.

INTRODUCTION

Phosphoric acid (H₃PO₄) is a medium-strong acid, but still shows strong corrosiveness on ferrous alloy (Jianguo et al., 1995). H₃PO₄ 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 H₃PO₄ 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 (Fouad and Sherbini, 1999; Bartos and Hackerman, 1992; Zucchi et al., 1992; Elachouri et al., 1995; Mernari et al; 1998; Bentiss et al., 2002; Elkadi et al., 2000; Walker and Richardson, 1980; Kertit and Hammouti, 1996; El Azhar et al., 2001; Tang et al., 2003; Zhang et al., 2003; Tadros and Abdenaby, 1988; Chin and Nobe, 1971; Agrawal and Namboodhiri, 1972; Eldakar and Nobe, 1976) among them nitrogen (N) containing inhibitor is one of the focuses of the studies (Bentiss et al., 2000). Bentiss et al. (2002), El Azhar et al. (2001) Lewis (1982), Li and Tang (2005) and Elkadi et al.

(2000) have investigated many N containing inhibitors for the corrosion inhibition of steel in hydrochloric acid (HCl) and tetraoxosulphate vi acid (H₂SO₄), their studies showed that, N containing organic inhibitor acts as a strong inhibitor for steel in HCl, compared with H₂SO₄. Triazole and triazole-type compounds containing N, sulphur (S) and heterocycle on the corrosion inhibition of metal in acidic media have attracted more attention because of their excellent corrosion inhibition performance (Qafsaoui and Takenouti, 2010; Finsgar and Milosev, 2010; Zheludkevich et al., 2005; Bentiss et al., 2000). The researches by Fouda and Ellithy (2009) showed that some 4-phenylthiazole derivatives could inhibit the corrosion of 304L stainless steel in Hcl solution, but the inhibition effect was not very excellent (Hui-Long et al., 2004; Abdallah et al., 2012).

However, synergistic effect occurred on addition of Potassium thiocyanate (KSCN) to the acid containing 4-phenylthiazole derivatives which inhibited 304L stainless steel corrosion, and the phenomenon of synergism took place at very low concentrations for the systems studied. Wang et al. (2012) also investigated the effect of some mercapto-triazole derivatives synthesized containing different hetero atoms and substituents in the organic structures on the corrosion and hydrogen permeation of mild steel in Hcl solution and their results revealed that all the mercapto-triazole derivatives performed excellently

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as corrosion inhibitors. Especially, some N-and S-containing triazole derivatives are environmentally friendly corrosion inhibitors compared with some commercial acid corrosion inhibitors which are highly toxic, such as chromate and nitrite (Bentiss et al., 1999). Little work appears to have been done on the inhibition of carbon steel in H_3PO_4 solution. In this work, benzothiazole derivatives containing N, S and aromatic ring had been studied on the corrosion inhibition of carbon steel in H_3PO_4 solutions by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques.

EXPERIMENTAL METHOD

Materials preparation

The chemical composition of carbon steel (wt %) was as follows: 0.200 C, 0.350 Mn, 0.024 P, 0.003 Si and the remainder Fe. Seven pieces of carbon steel were cut into $2\text{ cm} \times 2\text{ cm} \times 0.2\text{ cm}$. The specimens were polished with a series of emery papers of different grit size up to 1200, degreased in acetone (Zheludkevich et al., 2005), rinsed with bi-distilled water and finally dried between two filter papers and then weighed.

After which the specimens were immersed in 100 ml solution of H_3PO_4 without and with different concentrations of the studied inhibitors for 3 h at temperature range from 25-55°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

Potentiodynamic polarization, EIS, and EFM techniques were used for electrochemical measurements and the cell used was a conventional three electrodes Pyrex glass with a platinum foil counter electrode and a standard calomel electrode (SCE) as reference. The working electrode was carbon steel electrode, which was cut from carbon steel sheets with thickness of 0.1 cm. The electrode was of dimensions $1 \times 1\text{ cm}$ and was welded from one side to a copper wire used for electric connection.

The sample was embedded in a glass tube using epoxy resin (Fouda et al., 1990). 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 current-potential curves were recorded by changing the electrode potential automatically from - 500 to + 500 mV with a scan rate of 5 mV s^{-1} . Experiments for 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 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 (Fouda and Ellithy 2009). The electrochemical 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, and molecular weight of the investigated compounds, which has been labeled as A, B, and C. The synthesis and characterization (spectral measurements) of the PAMT was described and documented elsewhere previously (Sahin et al., 2002). Appropriate concentration of H_3PO_4 acid was prepared and diluted by bi-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). Figure 1 shows the weight loss-time curves for carbon steel corrosion at different concentrations of inhibitor, A is the most effective one at 25°C. Similar curves were obtained for other compounds (not shown). The curves obtained shows that the weight loss of carbon steel in presence of inhibitor is lower than free inhibitor and decreases with increasing inhibitors concentrations (Bentiss et al., 2002). This means that these compounds act as inhibitors for carbon steel in H_3PO_4 solutions. The degree of surface coverage (θ) and the inhibition efficiency ($\% \eta$) were calculated using the following equation:

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

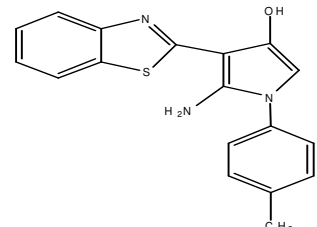
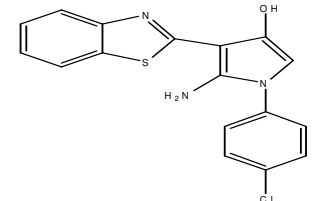
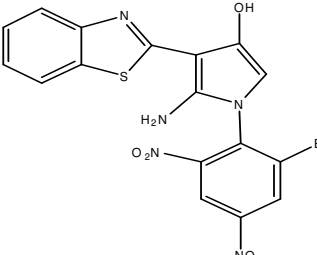
Where, W_{inh} and W_{free} are the weight losses per unit area in the presence and absence of the inhibitors, respectively. Values of $\% \eta$ are listed in Table 2. The values of the inhibition efficiency increases with increase in the inhibitor concentration. This behavior could be attributed to 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:

$$A > B > C.$$

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 (θ) corresponding to different concentrations of the inhibitor have been used to determine the adsorption isotherm. The variation of surface coverage (θ) determined by weight loss with the logarithm of the inhibitor (A) concentration $\log C$, at different temperatures is represented in Figure 2. Similar curves were obtained for other inhibitors (not shown). The linear relationships of θ vs. $\log C$ depicted in

Table 1. The chemical structure of the investigated benzothiazole derivatives.

Component	Structure	Names, molecular formula	Molecular weight
A		5-amino-4-(benzo[d]thiazol-2-yl)-1-p-tolyl-1H-pyrrol-3-ol C ₁₈ H ₁₅ N ₃ OS	321.40
B		5-amino-4-(benzo[d]thiazol-2-yl)-1-(4-chlorophenyl)-1H-pyrrol-3-ol C ₁₇ H ₁₂ ClN ₃ OS	341.81
C		5-amino-4-(benzo[d]thiazol-2-yl)-1-(2-bromo-4,6-dinitrophenyl)-1H-pyrrol-3-ol C ₁₇ H ₁₀ BrN ₅ O ₅ S	476.26

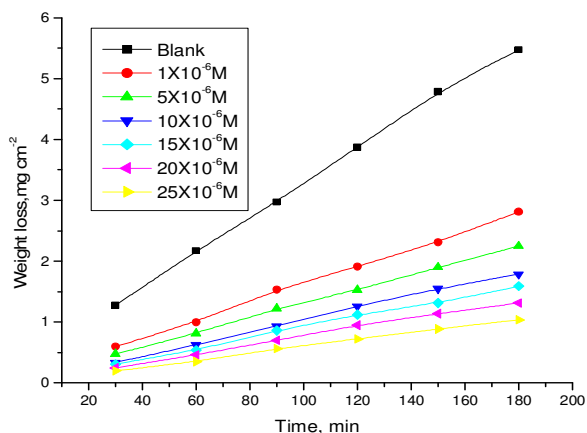
**Figure 1.** Weight loss-time curves for the dissolution of carbon steel in the absence and presence of different concentrations of inhibitor (A) in 1 M H₃PO₄ at 25°C.

Figure 2 with correlation coefficient nearly equal to 1.0 ($R^2 > 0.9$) suggest that the adsorption of benzothiazole derivatives from 1 M H₃PO₄ solution on carbon steel obeys the Temkin adsorption isotherm. According to this isotherm the surface coverage is related to inhibitor concentration by:

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

Table 2. Inhibition efficiency (% η) at different concentrations of inhibitors for the corrosion of carbon steel after 180 min immersion in 1 M H₃PO₄ at 25°C.

Concentration (μM)	(A) % η	(B) % η	(C) % η
1	48.3	32.7	26.1
5	50.8	51.6	34.9
10	70.6	58	50
15	72.7	62.2	58.4
20	77.3	68.1	63.4
25	81.1	70.6	65.1

Where "a" is the molecular interaction parameter and K_{ads} is the equilibrium constant of the adsorption process. The free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ was calculated from the following equation (Bentiss et al., 2002):

$$\Delta G^{\circ}_{\text{ads}} = -RT \ln(55.5K) \quad (3)$$

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 $\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - T\Delta S^{\circ}_{\text{ads}}$ and plot $\Delta G^{\circ}_{\text{ads}}$ versus T linear relationships with slope equal ($-\Delta S^{\circ}_{\text{ads}}$) and intercept of ($\Delta H^{\circ}_{\text{ads}}$) were obtained. The data were collected in Table 3. From data in Table 3 we can

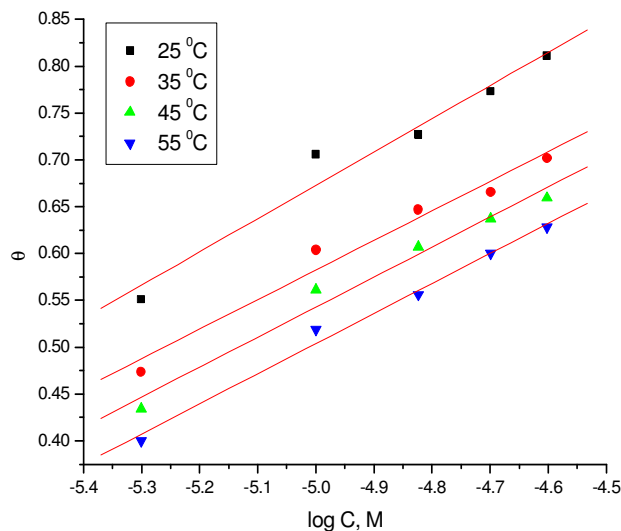


Figure 2. Temkin adsorption isotherm for carbon steel in 1 M H_3PO_4 in the presence different concentrations of inhibitor (A) at different

Table 3. Thermodynamic parameters for the adsorption of benzothiazole derivatives on carbon steel surface in 1 M H_3PO_4 at different temperatures.

Temperature °C	$K_{ads} \times 10^{-6}$ M ⁻¹	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{ads}$ kJ mol ⁻¹	ΔS°_{ads} J mol ⁻¹ 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		

conclude that:

i) Negative sign of ΔG°_{ads} indicates that the adsorption of benzothiazole derivatives on carbon steel surface is proceeding spontaneously (El-Awady et al., 1992; Abd El-Rehim et al., 2001).

ii) Generally, values ΔG°_{ads} of up to -20 kJ mol^{-1} are consistent with physisorption, while those around -40

kJ mol^{-1} 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 ΔG°_{ads} the existence of comprehensive adsorption (physisorption and chemisorption) was found (Li et al., 2005), that is to say, since the adsorption heat approached the general chemical reaction heat, the chemical adsorption occurs.

iii) Negative sign of ΔH°_{ads} indicates that the process of adsorption is exothermic.

iv) Positive sign of ΔS°_{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 be desorbed from the metal surface by one inhibitor.

Effect of temperature

The effect of temperature on corrosion inhibition of carbon steel in 1 M H_3PO_4 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_3PO_4 solution in the absence and presence of different concentrations of benzothiazole derivatives were calculated from Arrhenius type equation (Putilova et al., 1960):

$$\log k_{corr} = \log A - E^*_a / (2.303RT) \quad (4)$$

Where, A is the Arrhenius pre-exponential factor. A plot of $\log k_{corr}$ versus $1/T$ gave straight lines as shown in Figure 3. The enthalpy of activation (ΔH°) and the entropy of activation (ΔS°) were obtained by applying the transition-state equation:

$$\log (k_{corr}/T) = [\log(R/Nh) + (\Delta S^{\circ} / 2.303R) - (\Delta H^{\circ} / 2.303RT)] \quad (5)$$

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

i) 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.

ii) 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.

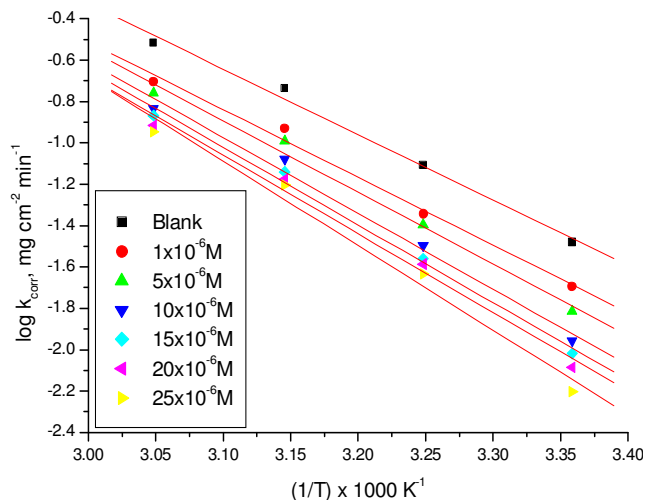


Figure 3. Arrhenius plots for carbon steel dissolution in 1 M H_3PO_4 in the absence and presence of different concentrations of inhibitor (A).

- iii) Values of ΔH^\ddagger are positive. This indicates that the corrosion process is an endothermic one.
- iv) The entropy of activation (ΔS^\ddagger) 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 (Li et al., 2005).

Electrochemical techniques

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. Figure 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 (I_{corr}), the corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), degree of surface coverage (θ), and the inhibition efficiency η_{Tafel} (%) were calculated from Equation 7 and were given in Table 5.

$$\eta_{Tafel}\% = [1 - (I_{corr} / I_{corr}^0)] \times 100 \quad (6)$$

Where I_{corr}^0 and I_{corr} correspond to uninhibited and inhibited corrosion current densities, respectively. The results indicate:

- i) The cathodic and anodic curves obtained exhibit Tafel-type behavior. Additional of benzothiazole derivatives

increased both the anodic and cathodic overvoltages

- ii) The corrosion current density (I_{corr}) decreases with increasing the concentrations of the benzothiazole derivatives which indicates that these compounds acts as inhibitors, and the degree of inhibition increases with increasing the inhibitor concentration.

The slopes of the anodic and cathodic Tafel lines (β_a and β_c) were slightly changed on increasing the concentration of inhibitors and are parallel. This indicates that there is no change in the mechanism of the inhibition in presence and in absence of inhibitors. The benzothiazole derivatives exhibit mixed-type inhibitors (Jeyaprabha et al., 2005; Amin et al., 2007), 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 the surface kinetic process rather the diffusion-controlled process.

- iii) The order of inhibition efficiency of all inhibitors at different concentrations given by polarization measurements are listed in Table 5. The results are in good agreement with that obtained from weight-loss measurements. The difference of inhibition efficiency from the two methods may be due to the difference in measurement time taken for different techniques. Weight loss study is long term method requires 3 h, while electrochemical techniques are short term method that takes 30 min only. The inhibition efficiency values obtained from Tafel curve measurements may be due to the fact that Tafel measurements are carried out by applying a potential of ± 250 mV.

Electrochemical impedance spectroscopy technique (EIS)

EIS 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. Figure 6, 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 Bode plots (Figure 7) revealed that each impedance diagram consists of a large capacitive loop with one capacitive time. The equivalent circuit model which describes the metal/electrolyte interface of the present corroding system is shown in Figure 8, where R_s , R_{ct} and CPE refer to solution resistance, charge transfer resistance and constant phase element, representing the double layer capacitance (C_{dl}) of the interface, respectively. The R_{ct} is calculated from the difference in impedance at lower and higher frequencies (Ross Macdonald 1987). The double layer capacitance (C_{dl}) was calculated using Equation 8 (Abd El-Rehim, 1999).

$$C_{dl} = 1 / (2 \pi f_{max} R_{ct}) \quad (7)$$

The inhibition efficiencies obtained from the EIS measurements are calculated from the relation (Zucchi et al., 1992).

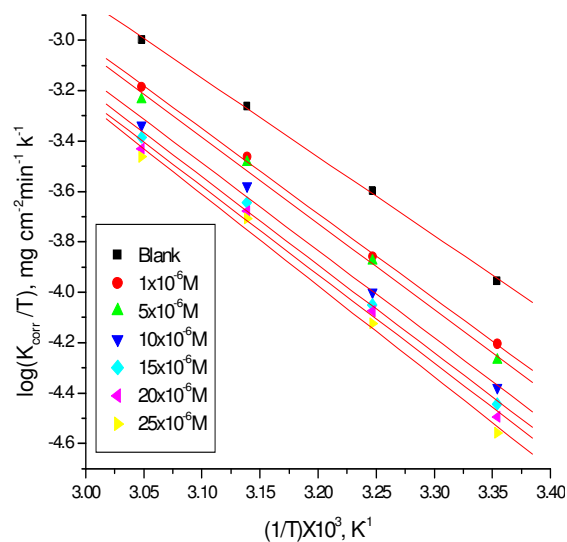


Figure 4. Transition state plots for carbon steel dissolution in 1 M H_3PO_4 in the absence and presence of different concentrations of inhibitor (A).

$$\% \eta = [1 - (R_{ct} / R'_{ct})] \times 100 \quad (8)$$

Where R_{ct} and R'_{ct} are the transfer resistance without and with the inhibitor, respectively.

In fact, the presence of inhibitors enhances the value of R_{ct} in acidic solution indicating a charge-transfer 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:

- i) R_{ct} increased by increasing the concentrations of benzothiazole derivatives giving consequently a decrease in the corrosion rate.
- ii) 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 (Fouda and Ellithy, 2009).
- iii) I_{corr} values decrease significantly in the presence of these additives and the $\% \eta$ is greatly improved. The order of reduction in I_{corr} exactly correlates with that obtained from potentiostatic polarization studies.
- iv. 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 EIS measurements are in good agreement.

Electrochemical frequency modulation (EFM)

Several authors proposed EFM as a new electrochemical

technique for online corrosion monitoring (Khaled, 2005, 2008; Jones, 1983; Bosch et al., 2001). 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. 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 inter-modulation 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.

Figures 9 to 13 show that, the current response contain 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 (β_a and β_c) and the causality factors (CF-2 and CF-3). These electrochemical corrosion kinetic parameters at different concentrations of inhibitors in 1 M H_3PO_4 at 25°C were simultaneously determined and are listed in Table 7. The inhibition efficiency $\% \eta$ calculated from Equation 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 N, O and S atoms, π -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 co-ordination affinity toward N, O, and S bearing ligand. Hence, adsorption on carbon steel can be attributed to co-ordination through hetero-atoms and π -electrons of aromatic rings (Ahmad et al., 2010). In all investigated benzothiazole derivatives, there are unshared electron pairs on N, O, and S, capable of forming σ -bond with carbon steel. Further, the double bonds in the molecule allow back donation of metal d-electron to the π^* -orbital. Another striking feature for high inhibition performance of all studied compounds is the presence of S-atom.

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	Concentration μM	$A \times 10^{-9}$ $\text{g cm}^{-2} \text{min}^{-1}$	E_a^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-S^*$ $\text{J mol}^{-1} \text{K}^{-1}$
Blank	-----	-----	60.7	60.0	71.6
	1	2.06	62.6	64.7	66.9
	5	6.91	66.3	65.4	59.4
	10	25.40	70.3	66.4	58.4
	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
A	1	2.93	61.9	62.7	67.2
	5	3.96	64.0	63.4	66.0
	10	17.80	68.6	64.0	65.4
	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
	B	1	1.34	61.5	61.8
5		2.35	63.0	62.3	67.9
10		8.79	66.4	63.4	65.8
15		7.20	66.80	65.10	61.60
20		7.78	67.80	65.60	61.00
25		12.4	68.70	66.40	60.20

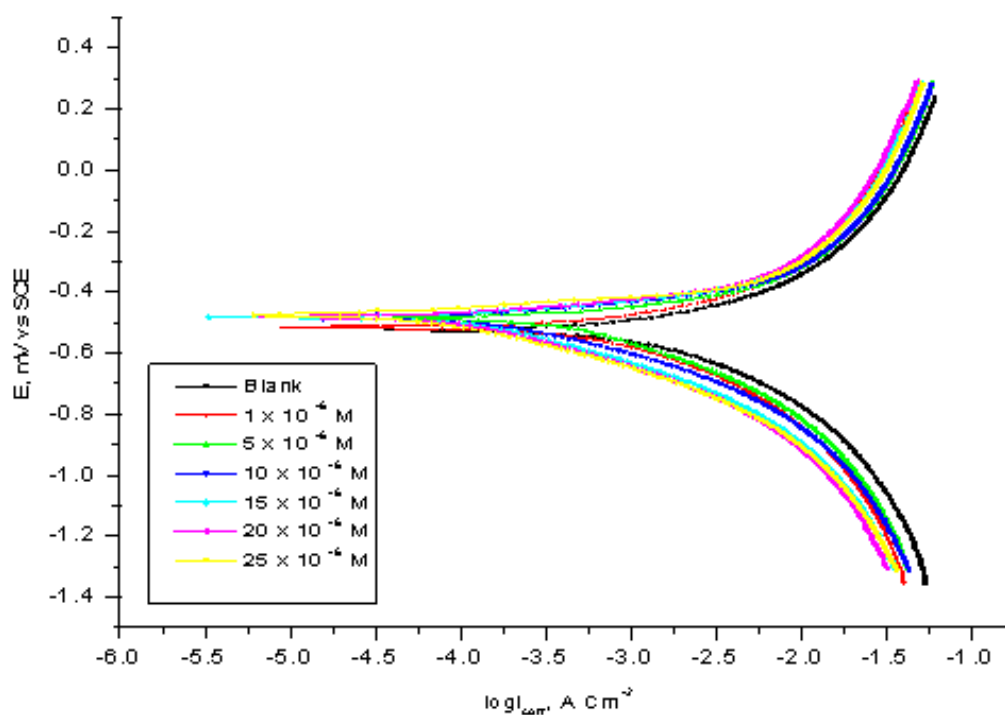
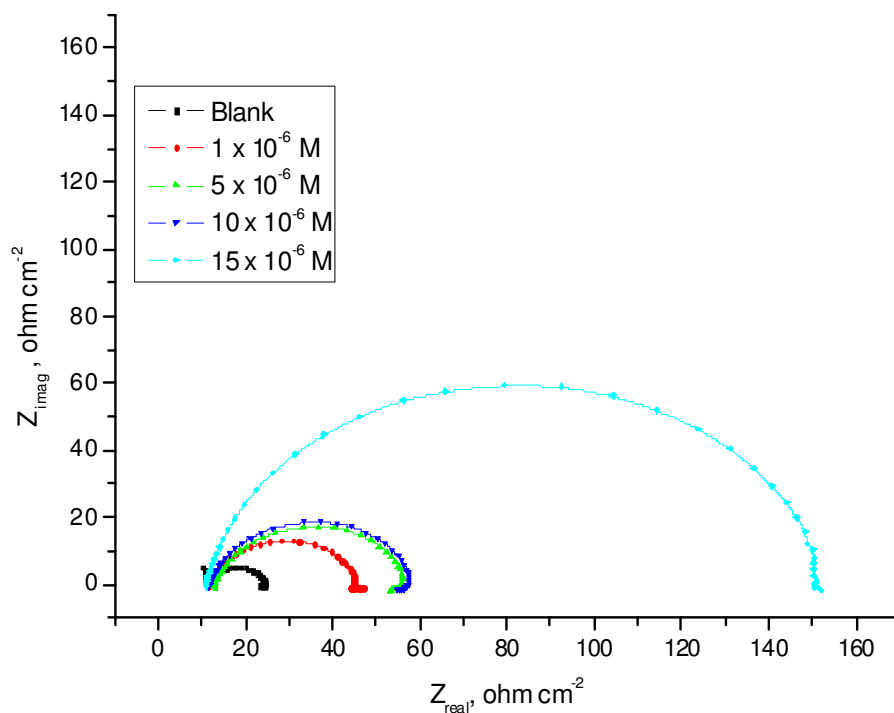


Figure 5. Polarization curves for the dissolution of carbon steel in 1 M H_3PO_4 in the absence and presence of different concentrations of inhibitor (A) at 25°C.

Table 5. Electrochemical kinetic parameters obtained from potentiodynamic polarization technique for the corrosion of carbon steel in 1 M H₃PO₄ at different concentrations of investigated inhibitors at 25 °C.

Inhibitor	Concentration μM	-E _{corr} , mV, vs SCE	I _{cor} mA cm ⁻²	-β _c mV dec ⁻¹	β _a mV dec ⁻¹	R _p Ω cm ²	θ	% η	CR mmy ⁻¹
Blank	0.0	524	5.527	767	648	27.6	-	-	64.152
A	1	516	2.566	634	535	27.6	0.536	53.6	29.787
	5	486	2.413	608	489	49.1	0.563	56.3	28.505
	10	480	1.087	471	393	48.8	0.836	83.6	10.512
	15	482	0.645	432	361	85.6	0.883	88.3	7.489
	20	481	0.522	420	351	132.5	0.906	90.6	6.602
	25	476	0.318	362	309	159.0	0.942	94.2	
B	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
	10	477	1.027	477	391	90.38	0.814	81.4	11.918
	15	477	0.737	446	369	119	0.867	86.7	8.552
	20	480	0.656	420	353	127.1	0.881	88.1	7.616
	25	482	0.470	408	343	172.1	0.915	91.5	5.452
C	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
	10	504	2.602	639	522	47.92	0.529	52.9	30.202
	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

**Figure 6.** Nyquist plots for carbon steel in 1 M H₃PO₄ solution in the absence and presence of different concentrations of inhibitor (A) at 25 °C.

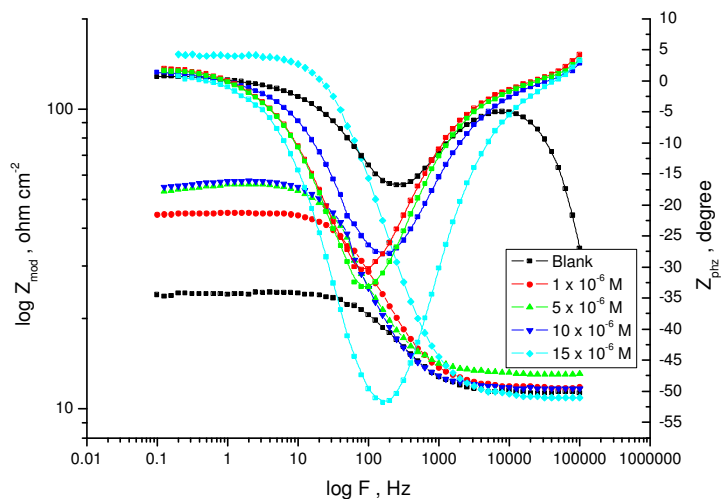


Figure 7. The bode plots for carbon steel in 1 M H₃PO₄ in the absence and presence of different concentrations of compound (A) at 25°C.

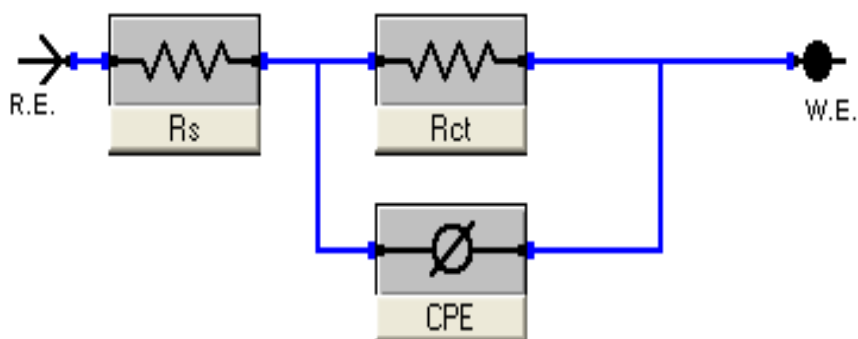


Figure 8. Electrical equivalent circuit used to fit the impedance data for carbon steel in 1 M H₃PO₄ solution.

Table 6. Electrochemical kinetic parameters obtained from EIS technique for the corrosion of carbon steel in 1 M H₃PO₄ at different concentrations of investigated inhibitors at 25°C.

Inhibitor	Concentration μM	$C_{dl} \times 10^{-3}, \mu\text{F cm}^{-2}$	$R_{ct}, \Omega \text{ cm}^2$	θ	% η
Blank	1 M H ₃ PO ₄	124.0	12.81	-	-
	1	60.0	33.65	0.619	61.9
	5	46.8	42.84	0.701	70.1
	10	44.8	45.72	0.720	72.0
	15	30.0	146.40	0.913	91.3
B	1	55.7	29.13	0.560	56.0
	5	49.1	32.43	0.605	60.5
	10	56.6	35.41	0.638	63.8
	15	57.7	85.46	0.850	85.0
C	1	96.1	27.06	0.527	52.7
	5	82.2	28.76	0.555	55.5
	10	50.9	31.27	0.590	59.0
	15	46.6	34.17	0.625	62.5

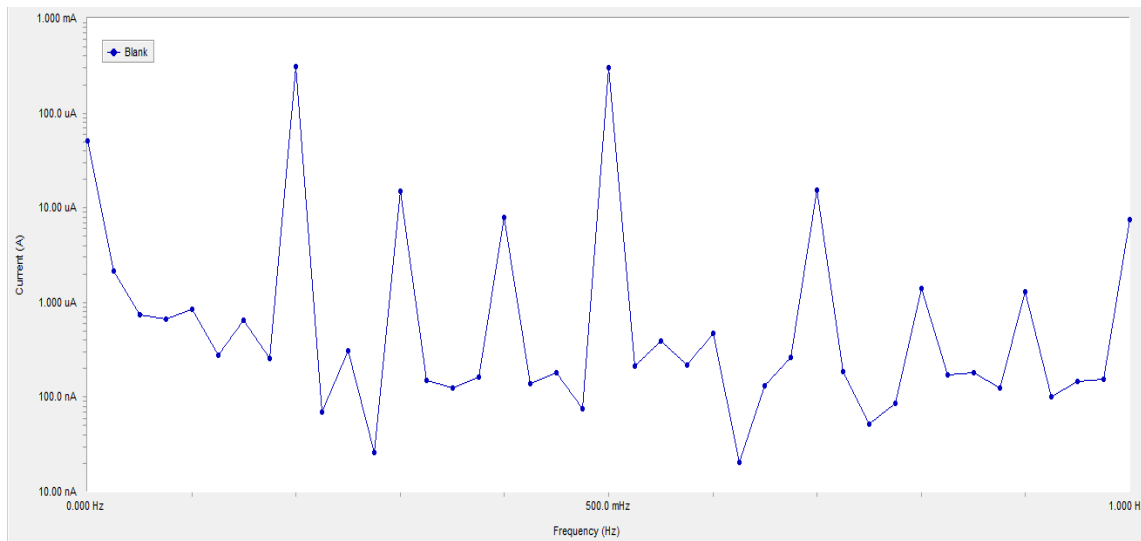


Figure 9. EFM spectra for carbon steel in 1 M H₃PO₄ (blank).

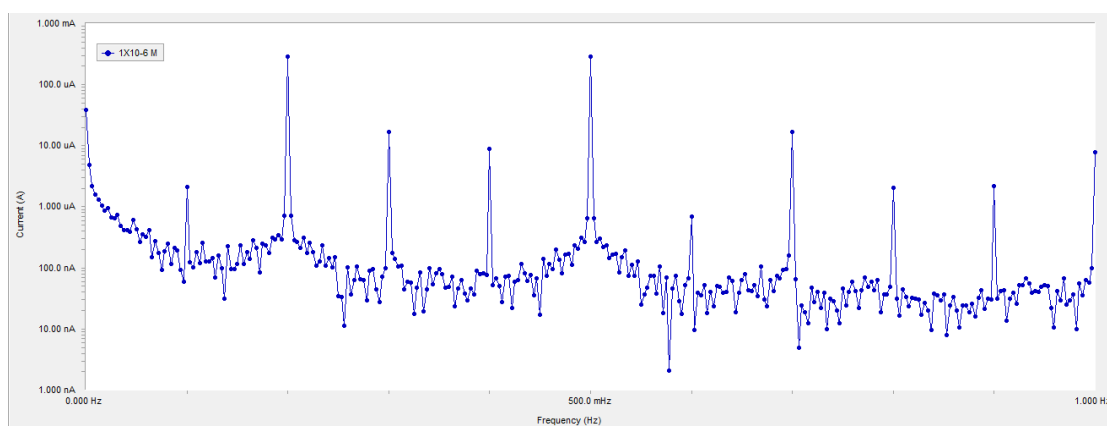


Figure 10. EFM spectra for carbon steel in 1 M H₃PO₄ in the presence of 1×10^{-6} M from inhibitor (A).

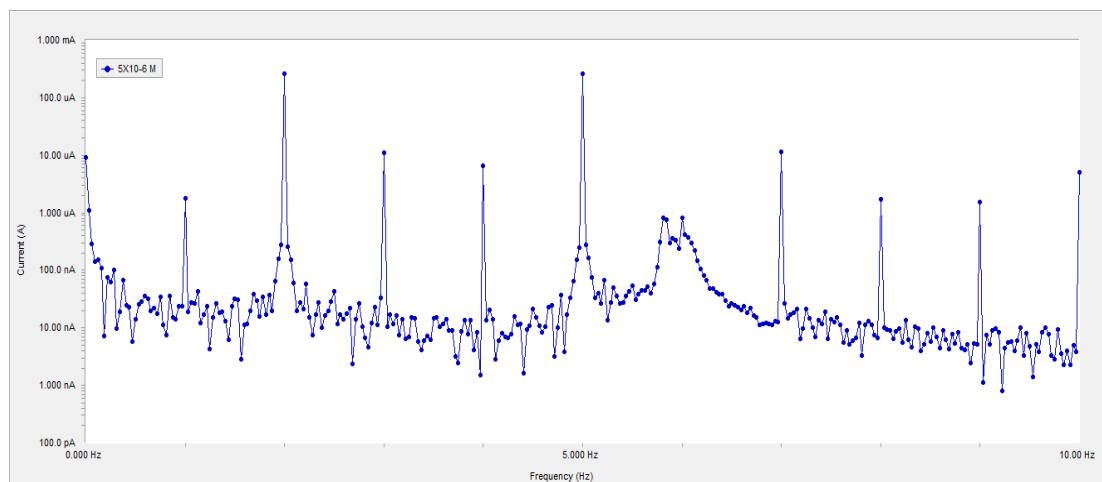


Figure 11. EFM spectra for carbon steel in 1 M H₃PO₄ in the presence of 5×10^{-6} M from inhibitor (A).

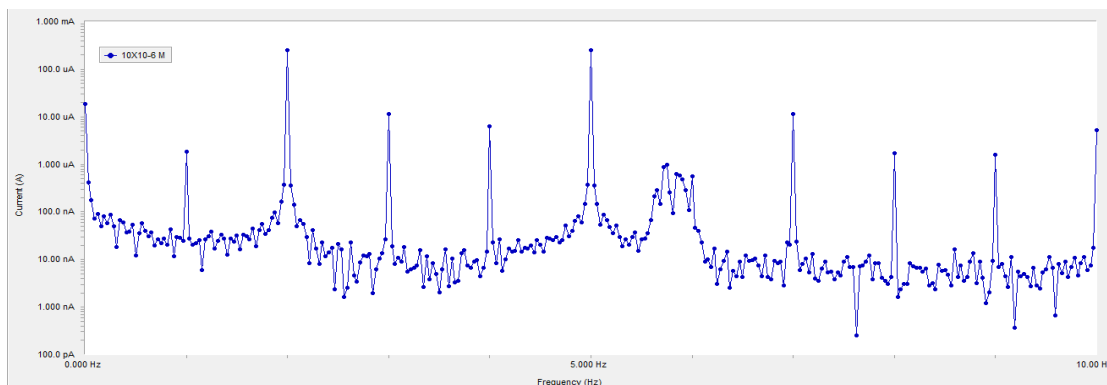


Figure 12. EFM spectra for carbon steel in 1 M H_3PO_4 in the presence of 10×10^{-6} M from inhibitor (A).

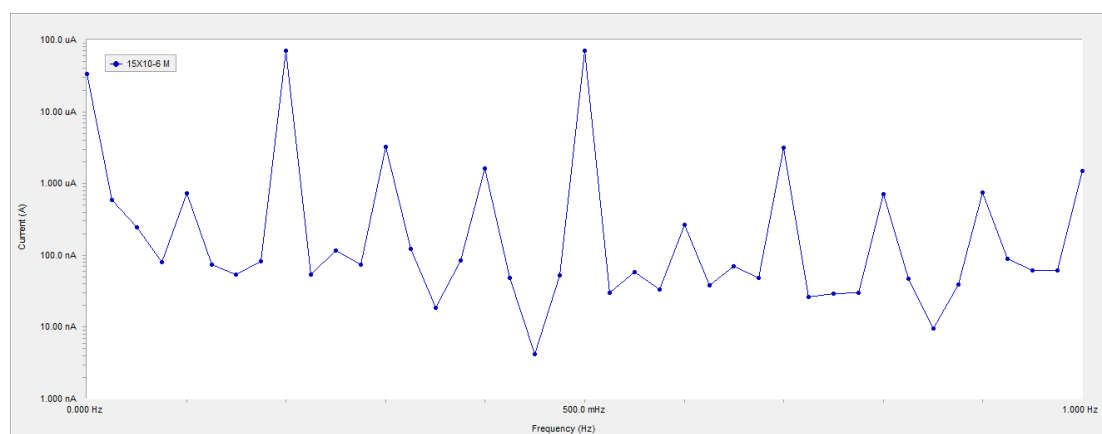


Figure 13. EFM spectra for carbon steel in 1 M H_3PO_4 in the presence of 15×10^{-6} M from inhibitor (A).

The presence of S-atom in the inhibitor structure makes the formation of $\text{d}\pi\text{-d}\pi$ bond resulting from the overlapping of 3d-electrons. From carbon steel, the 3d vacant orbital of S-atom become possible, this enhances the adsorption of the compounds on the metal surface. Also the lower solubility of S compounds and the greater polarizability of S 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 $\sigma = -0.17$) (Hammett, (1940)). The $-\text{CH}_3$ 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 chlorine (Cl) atom. So, compound (B) comes next to compound (A) in the order of Percentage inhibition and also, due to this, Cl atom acts as an electron withdrawing atom. Compound (C) is the least effective one; in spite of having the same number of

active sites (S, N, O atoms). This due to the presence of two nitro groups (NO_2) and one bromine (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_3PO_4 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 1M H_3PO_4 solution. Impedance studies indicated that R_{ct} values increased, while C_{dl} 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 through adsorption. The % η obtained from weight loss, polarization curves, electrochemical impedance spectroscopy and electrochemical frequency modulation are in good agreement.

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