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Mild Steel Surface Pretreatment Using Phosphoric acid-Inhibitor Solution

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ABSTRACT

In this study, a new mild steel surface pretreatment solution is introduced based on phosphoric acid containing a benzimidazole derivative as inhibitor. In this way, three different benzimidazole derivatives namely benzimidazole, 2-methyl benzimidazole and 2-aminobenzimidazole were studied in the 1M H_3PO_4 using DC and AC electrochemical techniques. Results revealed the better corrosion inhibition performance of 2-aminobenzimidazole in the acidic medium. EDS analysis revealed that surface elemental composition of oxygen and phosphorus increased after pretreatment process, that could be attributed to formation of some compounds based on iron phosphate. EIS diagrams of the painted substrates showed that pre-treated mild steel using phosphoric acid-inhibitor provided higher corrosion protection performance than untreated mild steel during immersion in 3.5% w/w NaCl solution. Furthermore, acid washing process enhanced adhesion and cathodic disbonding resistance of painted mild steel. Prog. Color Colorants Coat. 7(2014), 269-284 © Institute for Color Science and Technology.

1. Introduction

Acid Wash process is frequently utilized in many industries in order to cleaning and descaling of steel substrates [1, 2]. In this process, hydrochloric acid, phosphoric acid and sulfuric acid are used due to their special chemical properties [3]. Although phosphoric acid is more expensive than hydrochloric and sulfuric acids, it has higher capability of producing anticorrosive layer on the mild steel surface [4].

During phosphoric acid washing process, iron phosphates ($Fe_3(PO_4)_2$ and $FePO_4$) as polar products could be formed on the surface of steel sheet as a result of anode-cathode product reaction and the surface polarity of mild steel could be increased [4-7]. The anticorrosive performance, coating resistance against cathodic delamination and adhesion properties of coated substrate could be significantly affected after treatment [7]. Mineral acids are aggressive solutions for metallic substrates and using corrosion inhibitors is

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one of the most practical methods to prevent the corrosion attack during washing process [8, 9]. Different researches reported the corrosion inhibition properties of organic compounds containing oxygen, sulfur and nitrogen [10-12]. Replacement of common phosphoric acid inhibitors by eco-friendly compounds is a subject of current researches. Imidazole derivatives studied in this paper are eco-friendly and safe inhibitors and they could be efficient in acidic media due to their special chemical structures [13, 14].

In many industries, organic coatings are applied after acid washing process [2]. As a result, the effect of the surface treatment on the corrosion performance, cathodic disbonding resistance and adhesion strength of organic coating is an interest of engineers [15, 16]. Among organic coatings, powder coatings containing anticorrosive pigments are utilized in different industries specially pipeline protection. Different kinds of organic and inorganic pigments have been used to improve the anticorrosion performance of epoxy powder coatings. Chromates due to their excellent anticorrosion performances have widely used to improve the protection behavior of the epoxy coating. However, chromates are toxic and carcinogenic and environmentally regulations become stricter in recent years [17-19]. Attempts have been carried out to use environmentally friendly alternatives. Zinc phosphate (ZP) is an alternative and is frequently used in paint industries [20-22]. Combination of cathodic protection and organic coatings are used in order to ensure long-term protection of steel structures continuously exposed to an electrolyte [8]. Therefore, one of the most important requirements of the protective coatings is resistance against cathodic disbondment. Anti-corrosive performance, adhesion and cathodic disbonding resistance of organic coatings are vital parameters for a variety of organic coating systems. The disbonding is resulted from the loss of bond at the edge of holidays in the coating-substrate interface due to the high pH environment beneath the film as a net consequence of cathodic reactions [23-26].

In this work, the inhibition performance of three benzimidazole derivatives in phosphoric acid (1M) was studied using polarization test. Epoxy powder coating containing ZP was applied on the acid washed substrate and anticorrosive properties, adhesion and cathodic disbonding resistance of the system were evaluated.

2. Experimental

2.1. Sample preparation

2.1.1. Acid washing process

A laboratory grade phosphoric acid (1M) was purchased from Mojalali Co. Three imidazole derivatives including benzimidazole (BI), 2-methyl benzimidazole (2MBI) and 2-aminobenzimidazole (2ABI) were obtained from Merck and used without further purification. The chemical structures of the imidazole derivatives are shown in Figure 1.

St-37 type mild steel sheets (with dimension of 3×3× 0.6 cm) were prepared from Mobarake Steel Co with the following composition: $C \leq 0.1\%$, $Mn \leq 0.4\%$, $P \leq 0.05\%$, Fe remainder. The mill scale layer on the surface of mild steel sheets was carefully removed using a mechanical polisher (at 2000 rpm). Samples were then degreased by a commercial acetone solvent. Finally, 1 M phosphoric acid containing 2ABI was sprayed (Pressure = 2 bar) on the mild steel samples at 30°C for 45 s and then rinsed with deionized water.

2.1.2. Preparation of epoxy powder coatings

Epoxy powder coatings were prepared using ZP pigment (Table 1).

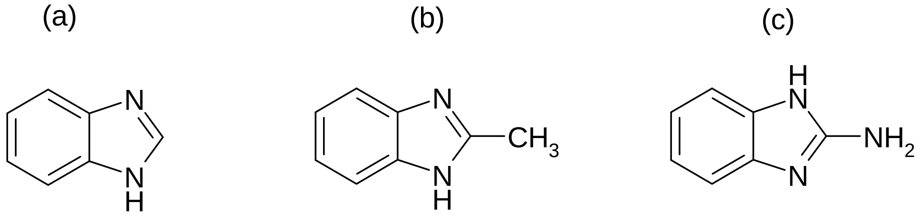

Figure 1: Chemical structure of inhibitors, (a) benzimidazole, (b) 2-methyl benzimidazole and (c) 2-aminobenzimidazole.

Table 1: The formulation of epoxy powder coating used in this work.

Component	w/w%
Epoxy Resine (Bisphenol A), EEW[†]=750	72.4
Hardener (Dicyandiamid)	3.9
Degasing Agent	0.49
Flow Agent	1.21
Wax	7
Pigment (ZP)	15

[†] Epoxy Equivalent Weight

The ZP pigment was prepared from Heubach Co. Epoxy powder coatings were applied over the pre-treated (acid washed) and bare samples using an electrostatic gun. Samples were cured at 180° C for 20 min. The dry film thickness (DFT) of the coatings was 30±5 µm.

2.2. Characterization

The anticorrosion performance of benzimidazole derivatives was studied using polarization technique. To this end, 1 cm^2 area of the sample was exposed to H_3PO_4 (1 M) containing different concentrations of benzimidazole derivatives. The test was performed using an AUTOLAB PGSTAT12 Equipment (at scan rate of 1 mVs^{-1}). Surface analysis of samples was examined by Energy Dispersive X-ray (EDS) analysis.

The anticorrosion performance of the epoxy powder coatings (on the surface of pre-treated and untreated samples) was studied by electrochemical impedance spectroscopy (EIS) in 3.5% w/w NaCl solution up to 63 days (AUTOLAB PGSTAT12). The test was carried out at open circuit potential (OCP) within frequency range of 10 mHz to 10 kHz (with the perturbation of 10 mV). FRA software was used to analyze the information obtained from EIS measurement. Both EIS and polarization tests were carried out in a three electrode electrochemical cell including reference electrode (saturated Ag/AgCl), auxiliary electrode (Pt) and working electrode (bare and coated sample). In order to evaluate cathodic disbonding of coated substrates, an artificial hole of 1 mm in diameter was drilled at the center of each sample. The test was carried at cathodic potential of -1.38 V vs. Ag/AgCl using magnesium sacrificial anode.

Pull-off adhesion testing of the coating was performed according to the procedure described in ASTM D 4541. The dollies of 20 mm diameter were degreased by acetone and then glued to the surface of the coated panels with two components epoxy based or a cyano-acrylate adhesive. After adhesive curing, a testing apparatus was attached to the loading fixture and was strained at 5 mm/min until the coating material had detached from the substrate. For each test, three replicate samples were employed, and the arithmetic average value is presented.

3. Results and discussion

3.1. Acid washing process

Inhibition performance of the benzimidazole derivatives at four concentrations (1×10^{-4}, 1×10^{-3}, 1×10^{-2} and 5×10^{-2} molar in H_3PO_4 (1 M)) was studied using DC polarization technique. Polarization curves of mild steel in H_3PO_4 (1 M, pH=1.09) in the absence and presence of BI, 2MBI and 2ABI at different concentrations were demonstrated in Figure 2. In order to complete adsorption of inhibitors on the metal surface, the polarization tests were carried out after 15 min immersion of steel plates in the phosphoric acid solution.

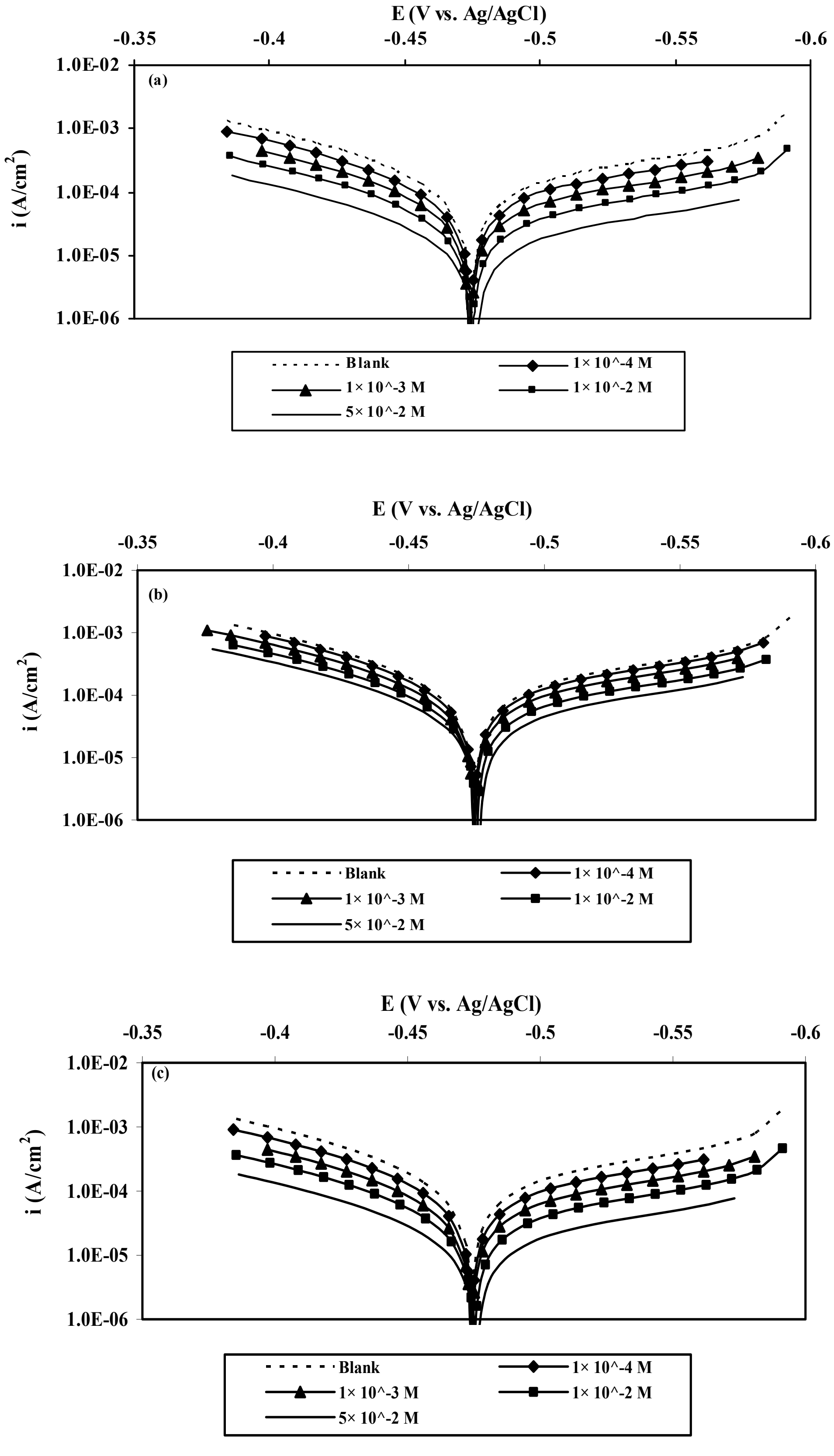

Figure 2: Polarization curves of mild steel in H_3PO_4 (1 M) containing (a) benzimidazole, (b) 2-methyl benzimidazole and (c) 2-aminobenzimidazole in different concentrations.

All imidazole derivatives show relatively similar behavior in polarization test. It is clear from Figure 2 that addition of inhibitors in the phosphoric acid damps the anodic and cathodic branches of the polarization curves resulting in decreasing the corrosion current density. This indicates that the inhibitors reduce the both anodic and cathodic reaction rates. All samples showed similar behavior in the polarization techniques, suggesting that the inhibitors had a mixed-type mechanism. The measured parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), inhibition efficiency (E%) and standard deviation of the corrosion current density (σ_I) were listed in Table 2.

Table 2: Electrochemical parameters of mild steel obtained from DC polarization test at various concentrations of imidazole derivatives in H_3PO_4 (1 M) at 298K.

	Concentration (M)	**E_{corr} (mV/Ag-AgCl)**	**I_{corr} ($\mu A/cm^2$)**	**E (%)**	**σ_I**
Blank	0	-474	392	-	2.1
BI	10^{-4}	-475	368	6.1	2.29
	10^{-3}	-476	323.4	17.5	2.51
	10^{-2}	-476	218.3	44.3	1.97
	5×10^{-2}	-477	148.9	62	2.02
2MBI	10^{-4}	-474	375.5	4.2	2.11
	10^{-3}	-474	327.3	16.5	1.95
	10^{-2}	-475	257	34.43	1.84
	5×10^{-2}	-476	174	55.60	2.12
2ABI	10^{-4}	-474	363.3	7.3	1.79
	10^{-3}	-474	289.2	26.20	2.01
	10^{-2}	-475	181.6	53.67	1.88
	5×10^{-2}	-476	120.4	69.28	1.96

Equation 1 measures the inhibition efficiency:

$$E\% = \frac{I_{Corr} - I_{Corr(inh)}}{I_{corr}} \times 100 \qquad \text{(Eq. 1)}$$

where $I_{corr(inh)}$ and I_{corr} are corrosion current densities with and without inhibitors, respectively which are determined by extrapolation of Tafel lines. The standard deviation of corrosion current density is calculated In Table 2 using Equation 2.

$$\sigma_I = \sqrt{\frac{\sum (I_i - I_{corr})^2}{(n-1)}} \qquad \text{(Eq. 2)}$$

where I_i is the corrosion current density calculated in each test, I_{corr} is the arithmetic mean of the corrosion current density presented in Table 2 and n is the number of the tests which is 3 in this study.

In order to confirm the results of DC polarizations, EIS technique was performed. Figure 3 shows the Nyquist diagrams of mild steel immersed in H_3PO_4 (1 M) containing different concentrations of the imidazole derivatives.

Considering the Nyquist plots of mild steel shows that addition of inhibitors increases the polarization resistance of the bare steel. The electrochemical parameters obtained from Nyquist diagrams using curve simulation of Figure 3 are presented in Table 3.

Table 3: Charge transfer resistance of mild steel obtained from DC polarization test at various concentrations of imidazole derivatives in H_3PO_4 (1 M) at 298K.

	Concentration (M)	R_{ct} (Ohm.cm^2)	σ_R
Blank	0	7.69	2.1
BI	10^{-4}	8.13	2.29
	10^{-3}	9.41	2.51
	10^{-2}	14.56	1.97
	5×10^{-2}	20.29	2.02
2MBI	10^{-4}	7.93	2.11
	10^{-3}	9.16	1.95
	10^{-2}	12.68	1.84
	5×10^{-2}	15.79	2.12
2ABI	10^{-4}	8.4	1.79
	10^{-3}	10.69	2.01
	10^{-2}	18.44	1.88
	5×10^{-2}	25.21	1.96

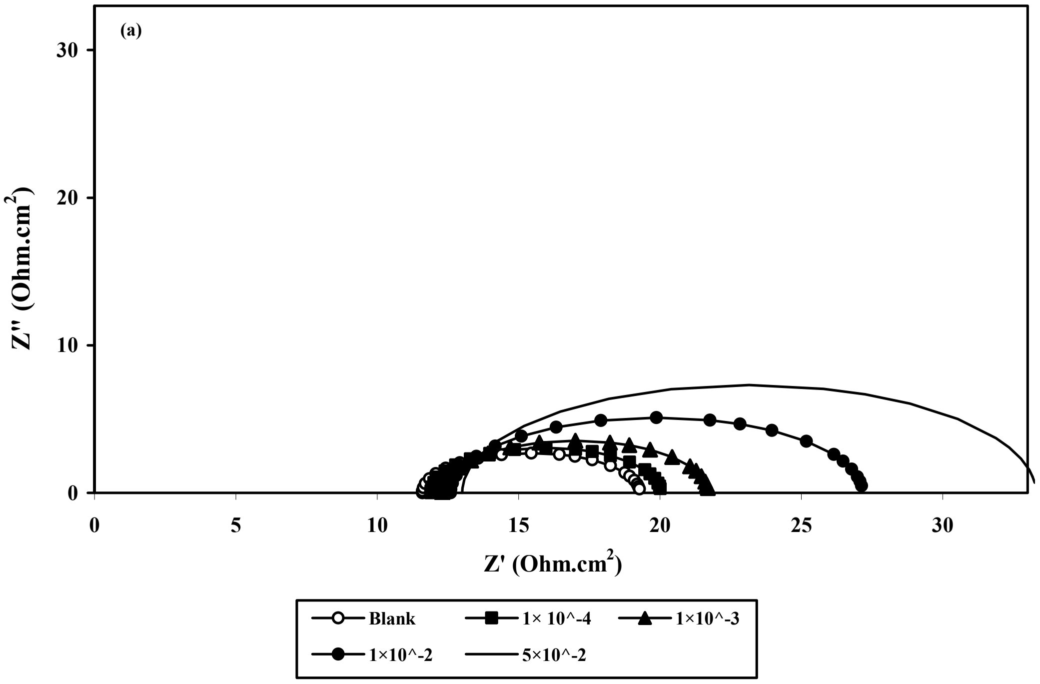

Figure 3: Nyquist diagrams of mild steel immersed in H_3PO_4 (1 M) containing different concentrations of (a) benzimidazole, (b) 2-methyl benzimidazole and (c) 2-aminobenzimidazole.

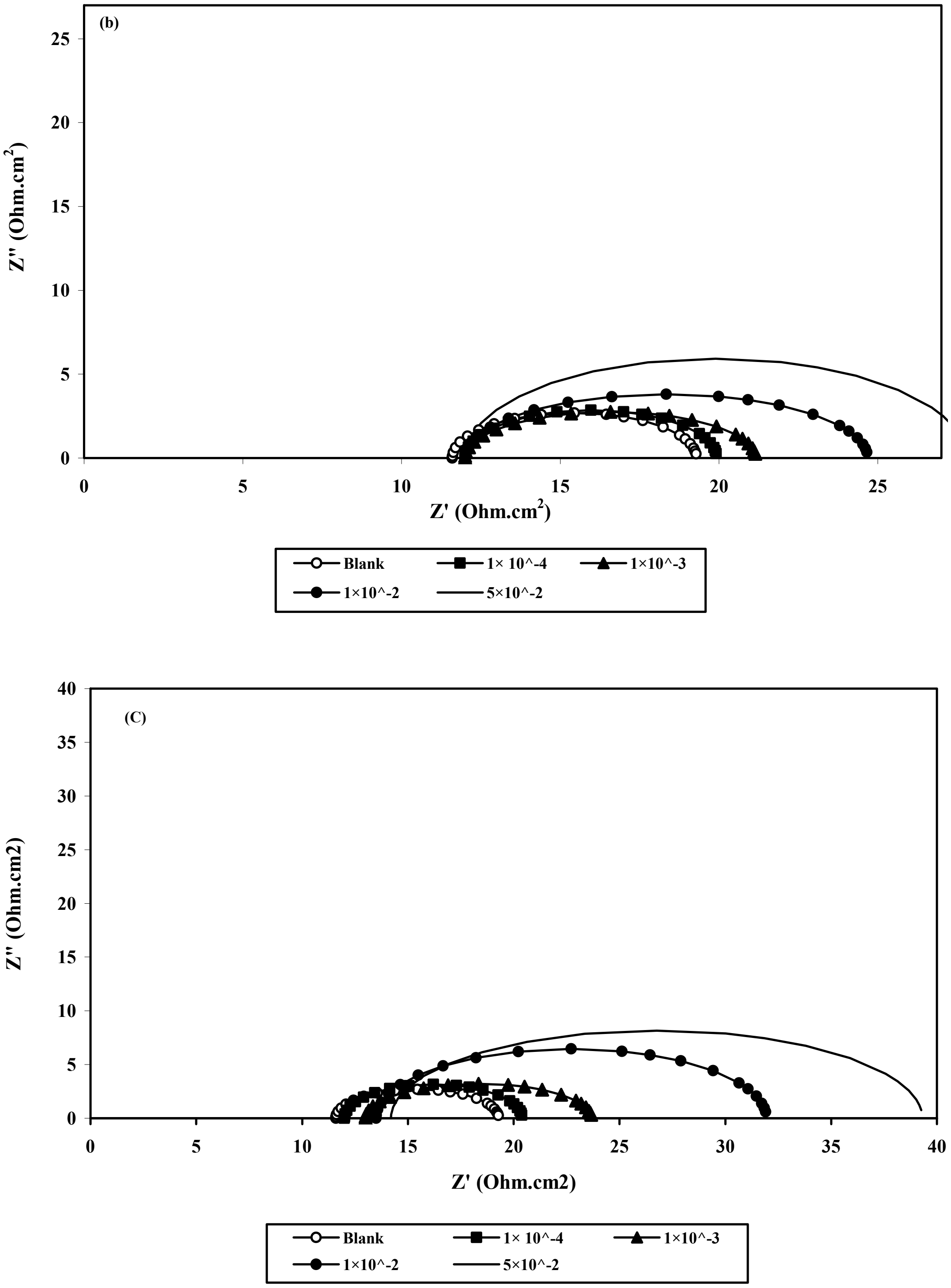

Figure. 3: Continued

As mentioned, σ represents the standard deviation of the obtained data which is calculated according to the method described in Equation 2.

As can be seen, increasing the inhibitor concentration leads to decrease in corrosion current density (I_{corr}) and increasing of charge transfer resistance (R_{ct}). Increasing the inhibitor concentration in phosphoric acid solution results in higher probability of inhibitor adsorption on the metal surface. Adsorption of the inhibitors reduces the cathodic reaction rate and results in the decreasing of the corrosion rate. Inhibition performance of the imidazole derivatives increases as follows: 2ABI>BI>2MBI. It is well-known that corrosion inhibition property of some organic compounds attributes to the oxygen, sulfur and nitrogen interaction of the chemicals with the base metal. These compounds can be physically and/or chemically adsorbed on the metal surface using lone electron pairs of oxygen, sulfur and nitrogen [2, 10]. This order could be attributed to the interaction between the lone pairs of nitrogen electrons of 2ABI molecule and the metal surface [2]. By considering the results of inhibition performance, pretreatment solution was prepared using H_3PO_4 (1 M) containing 2ABI (0.05 M).

The surface elemental composition of mild steel before and after acid washing process was studied using EDS analysis. Figure 4 shows the EDS diagram of the bare and the pretreated mild steel surface. It should be noted that the pretreatment solution was prepared from H_3PO_4 (1 M) containing 2ABI (0.05 M) and the effect of the surface acid washing pretreatment on the anticorrosion properties of the organic coating was evaluated based on this acid washing formulation. Surface elemental composition obtained from EDS spectrum are listed in Table 4.

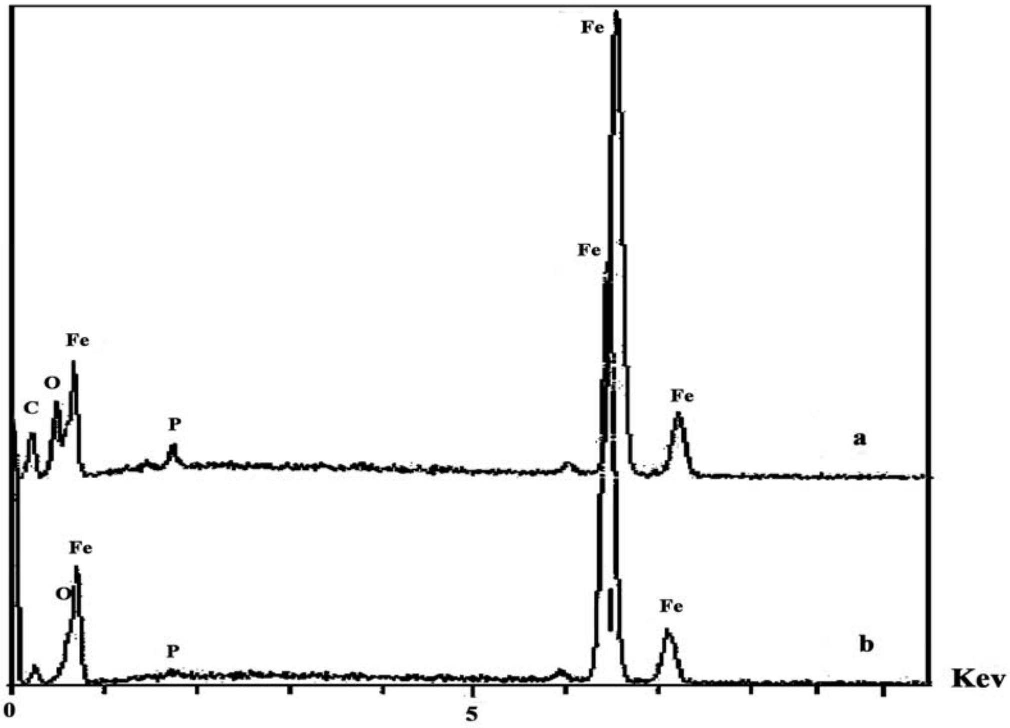

Figure 4: (a) EDX diagram of the bare and (b)the phosphoric acid washed mild steel surface

Table 4: Surface element composition obtained from EDS spectrum.

	Fe(%)	O(%)	P(%)	Other elements (%)
Bare mild steel	95.8	1.31	0.13	2.76
Phosphoric acid washed mild steel	94.38	3.31	1.73	0.58

Table 4 shows that the weight percentage of Fe, O and P on the surface increased after acid washing process. This could be attributed to the formation of a layer on the mild steel surface based on iron phosphate compounds. The following reactions (equations 3 to 8) could be taken place when the mild steel is exposed to acid washing solution [5-7].

Phosphoric Acid Dissociation:
$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$ Eq(3)

Anodic Reaction (1):
$Fe \rightarrow Fe^{2+} + 2e^-$ Eq(4)

Anodic Reaction (2):
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ Eq(5)

Cathodic Reaction:
$2H^+ + 2e^- \rightarrow H_2$ Eq(6)

Final Product (1):
$3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2$ Eq(7)

Final Product (2):
$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4$ Eq(8)

In order to evaluate the protective properties of the film formed on the mild steel, DC polarization and EIS tests were utilized. Figure 5 shows the polarization curves (a) and Nyquist diagrams (b) of the bare and acid washed mild steel samples exposed to 3.5% wt/wt NaCl solution.

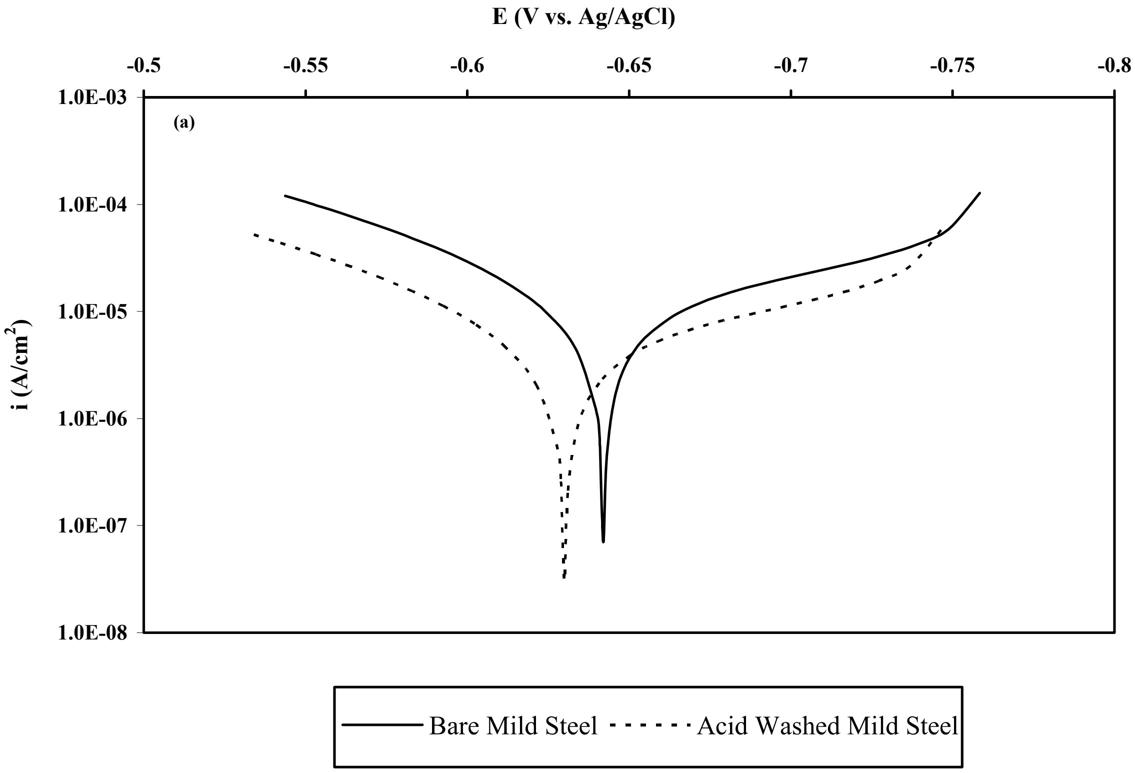

Figure. 5: (a) Polarization and (b) Nyquist diagrams of the bare and phosphoric acid washed mild steel in 3.5% NaCl solution

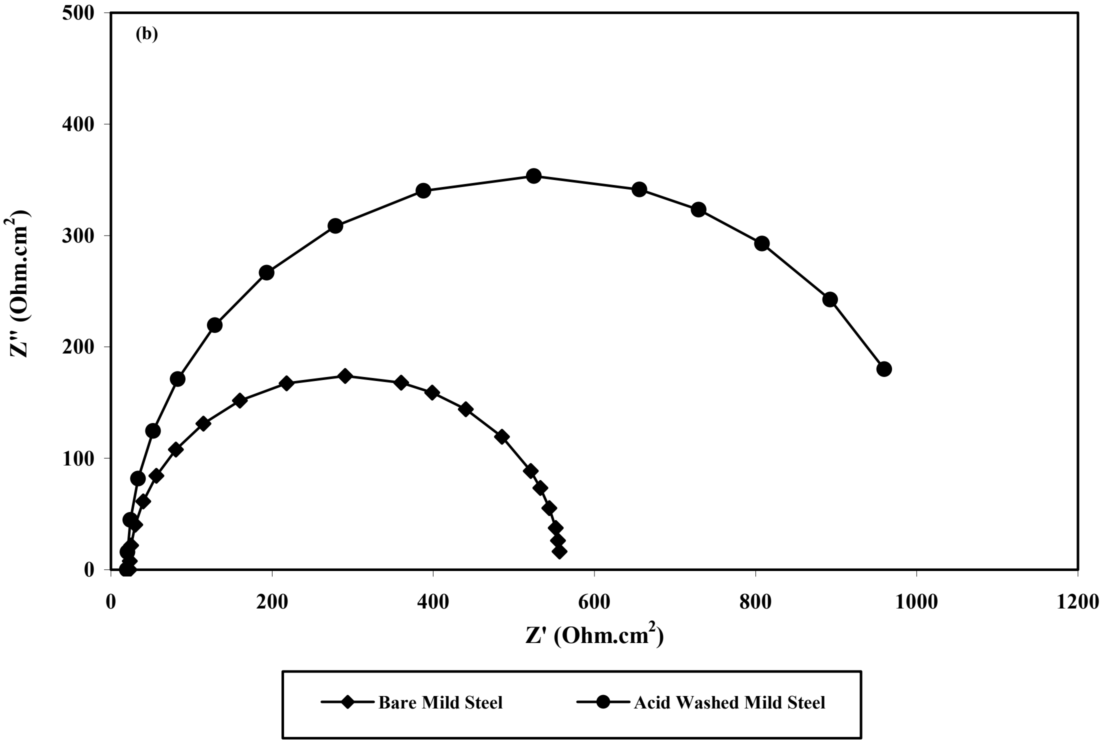

Figure. 5: Continued.

Table 5: Electrochemical parameters of the bare and phosphoric acid washed mild steel in 3.5% wt/wt NaCl solution.

	E_{corr} (mV/Ag-AgC)	I_{corr} (µA/cm^2)	σ_I	R_{ch} (Ohm.cm^2)	σ_{Rch}
Phosphoric acid washed mild steel	-630	4.47	0.453	1010	10.12
Bare mild steel	-642	8.91	0.501	535	9.13

The values of E_{corr}, I_{corr}, R_{ch}, σ_I and σ_{Rch} of the samples calculated from polarization curves using Tafel extrapolation (Figure 5.a) and Nyquist diagrams (Figure 5.b) were presented in Table 5.

Charge transfer resistance of the mild steel surface was calculated using an equivalent electrical model shown in Figure 6 (a) which its validity is confirmed in Figure 6 (b).

In the Figure 6 (a), R_s represents the electrolyte resistance, R_{ct} charge transfer resistance and C_{dl} double layer capacitance. According to Table 5, I_{corr} of mild steel sample decreases after acid pretreatment while R_{ch} increases.

As it has been previously demonstrated in Figure 4, a protective layer based on iron phosphates could be formed on the surface of mild steel sample after acid washing process. This layer can hinder the access of cathodic species to mild steel surface and consequently the corrosion current density will decrease. Table 5 shows that corrosion potential of mild steel shifted towards the noble potentials, indicating that acid washing inactivates the mild steel surface.

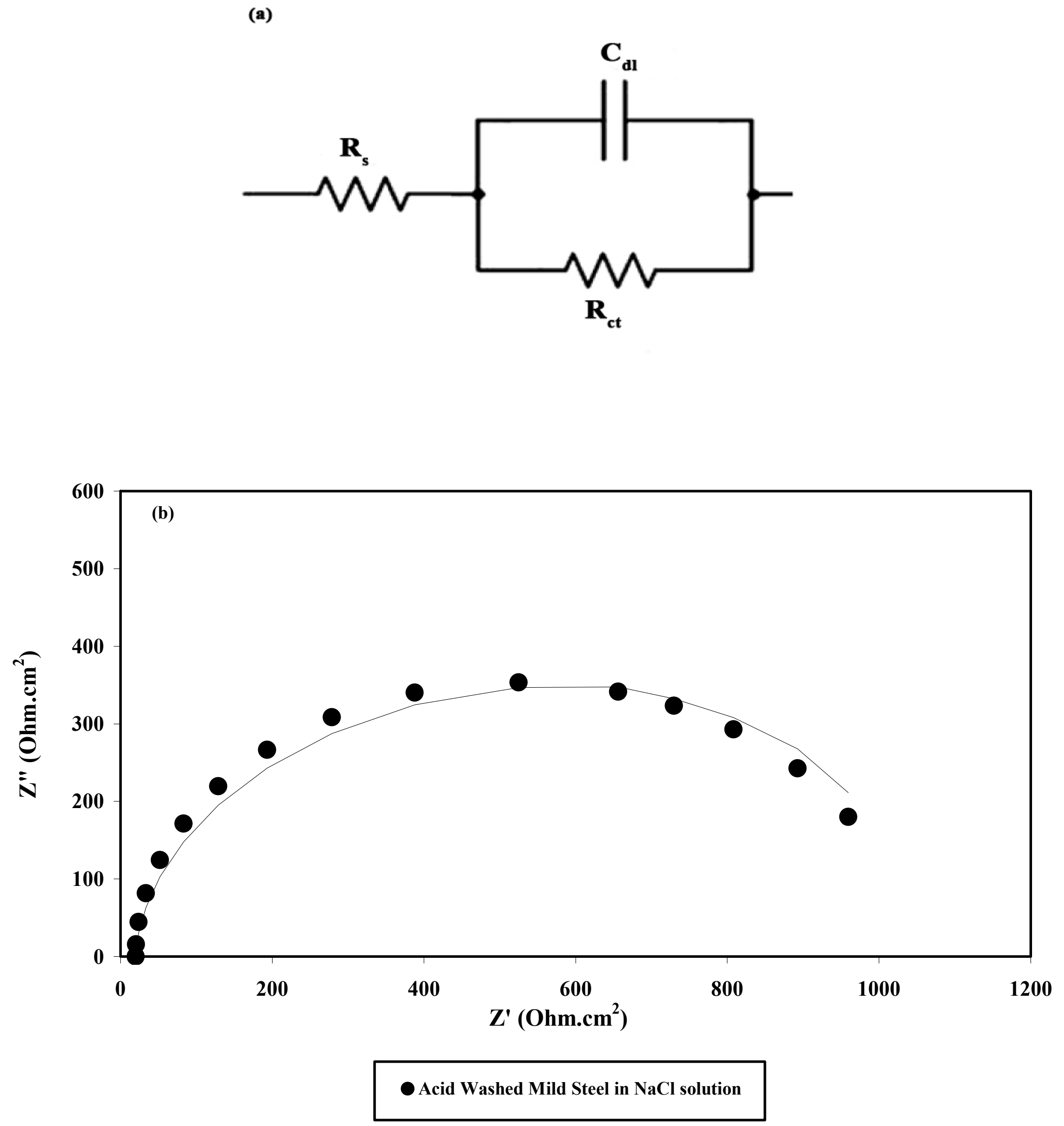

Figure. 6:(a). Equivalent electrical model of the bare mild steel and (b) comparison of the experimental data and fit curve of acid washed mild steel in 3.5% NaCl solution.

3.2. Epoxy powder coating

Epoxy powder coating containing ZP pigment was applied on the acid washed (ZP_P system) and bare mild steel (ZP_b system) surfaces to study the anticorrosion performance, adhesion and cathodic disbonding of the coatings.

The results of pull off adhesion test are presented in Table 6.

According to Table 6, acid washing process increases the adhesion of coating to the mild steel substrate. Based on EDS results, $Fe_3(PO_4)_2$ and $FePO_4$ could be formed on the surface of steel during the surface treatment (Eqs. (7) and (8)), so increasing the surface polarity. Increment of surface polarity could be resulted in the increasing of coating/metal adhesion.

Anticorrosive performance of the coating systems was studied by EIS. The Nyquist plots of the samples up to 63 days immersion in 3.5% wt/wt NaCl are shown in Figure 7.

Table 6: Results of pull off adhesion test for different coating systems.

	Pressure (psi)	σ_P
ZP_b	2800	20.11
ZP_p	3000	24.50

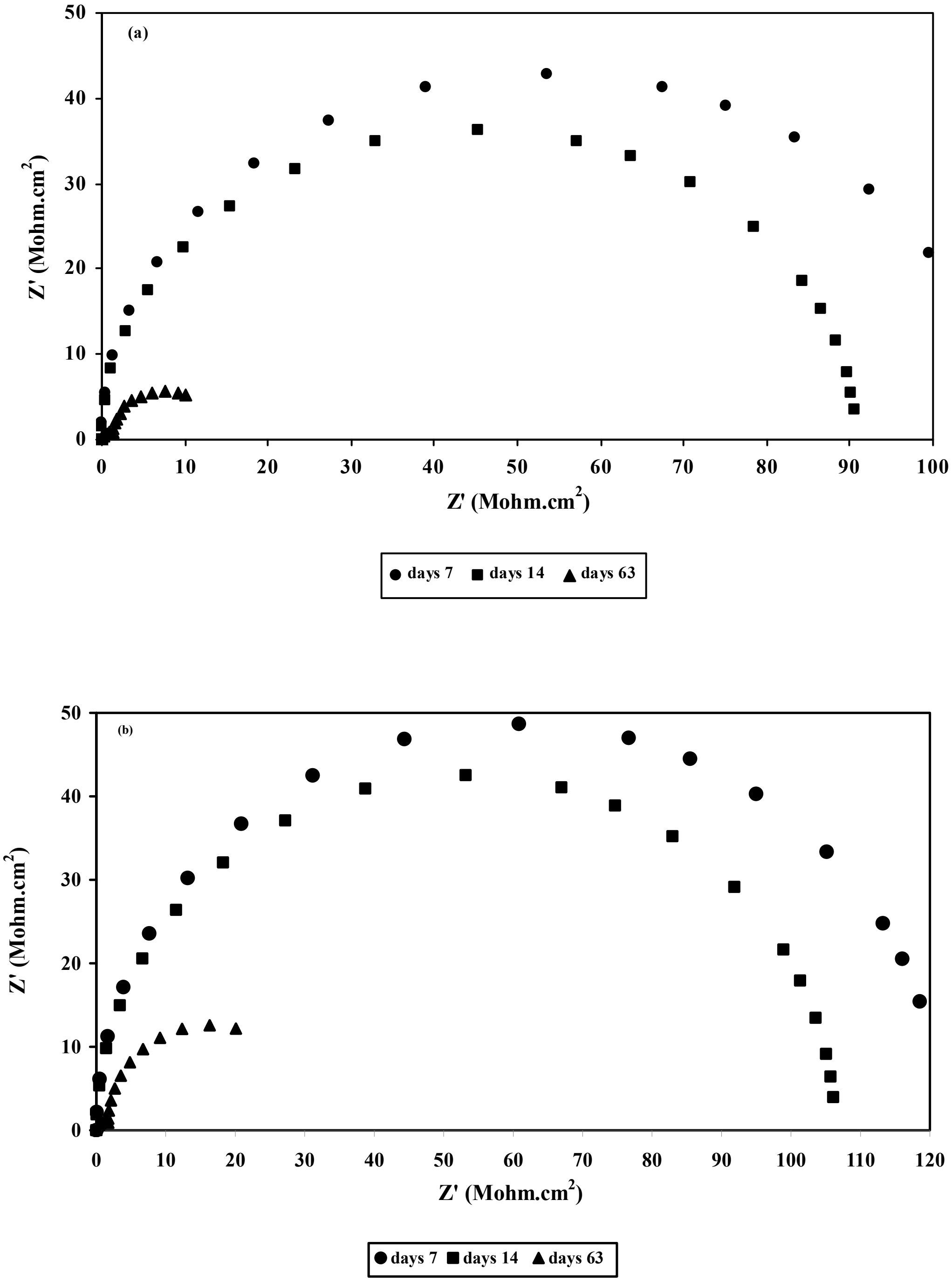

Figure. 7: (a)Typical Nyquist diagrams of ZP_b and (b) ZP_p coating systems in different immersion times in 3.5% NaCl solution.

Figure 7 demonstrates that one capacitive arc is observed for the coated substrates up to 14 days immersion. The impedance response reveals initial behavior that is dominated by the coating capacitance at high frequencies and coating resistance in the low frequency region. With increasing immersion time, the resistance decreased due to the penetration of water and the movement of ionic species through the coating layer, resulting in increasing the coating conductivity. Initially, the electrolyte penetrates through the coating film and sets up conducting pathways at various depths within the coating. Further, a second semicircle after 63 days immersion at low frequencies immerged in the EIS spectra, suggesting that electrochemical reactions at the metal/coating interface are progressing. At this stage, diffusion of the electrolyte into the coating is completed and the electrolyte phase meets the metal/oxide interface and corrosion reactions are occurred.

Using electrical model shown in Figure 8 (a), the Nyquist plots were fitted by AUTOLAB FRA software [18-21] (Table 7). Figure 8 (b) shows that experimental and fit curve are in good agreement with each other and the electrical model was correctly used.

In the Figure 8, $R_{coating}$ and $C_{coating}$ are coating resistance and coating capacitance, respectively. The coating and charge transfer resistances of the acid washed mild steel are higher than that of the bare one. These differences are more significant after 63 days immersion in the NaCl solution. This indicates that the surface treatment of mild steel increases the long-term corrosion performance of the paint system.

This may be attributed to the greater adhesion of epoxy coating to the acid washed sample compared to the bare sample. Coating with stronger adhesion bonds can significantly decrease the corrosion product formation as well as corrosion products spreading beneath the coating [13]. With less cathodic species spreading in the coating/metal interface, charge transfer resistance increases, results in better anticorrosive performance of the coating system.

The results of cathodic delamination can be correlated with the results of pull off adhesion test. By considering the fact that disbonding is due to the loss of adhesion bonds beneath the organic coating as a result of cathodic reaction [19-21], adhesion of coating to the substrate is a key parameter of organic coating delamination. The increment of the mild steel surface polarity results in the formation of a strong physical/chemical bonds at the coating/substrate interface, which in turn decreases the debonded area beneath the coating.

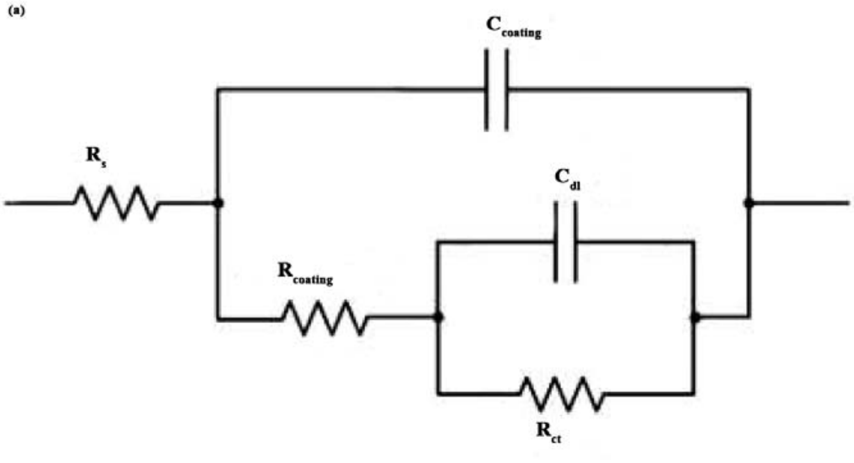

Figure 8: (a) Equivalent electrical model of coated mild steel and (b) comparison of the experimental data and fit curve for coated mild steel after 63 days immersion in 3.5% NaCl solution.

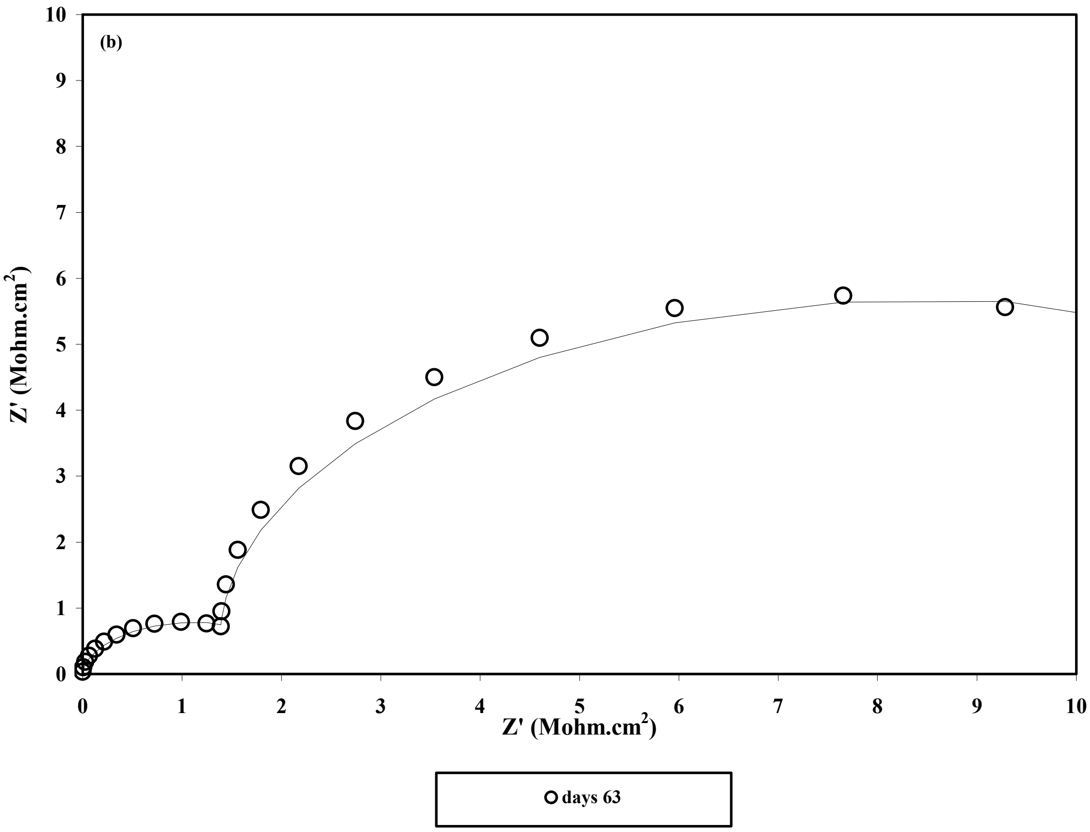

Figure 8: Continued

Table 7: Characteristic parameters evaluated from the impedance diagram for coating systems.

	Immersion time (Days)	$R_{coating}$ (Mohm.cm^2)	$\sigma_{R(coating)}$	R_{ct} (Mohm.cm^2)	$\sigma_{R(ct)}$	$C_{dl}\times10^8$ (F.cm^{-2})
ZP_p	7	121.7	3.75	-	-	-
	14	106.3	2.03	-	-	-
	63	2.42	0.12	29.22	1.12	8.44
ZP_b	7	107	2.11	-	-	-
	14	90.9	1.27	-	-	-
	63	1.98	0.09	12.53	1.25	10.05

Table 8: Disbonded area after 5 days immersion in 3.5% wt/wt NaCl for different coating systems.

	Disbonded Area (mm^2)	σ_{DA}
ZP_b	314	4.11
ZP_p	615	5.12

4. Conclusions

Corrosion inhibition performance of three benzimidazole derivatives in H_3PO_4 (1M) was studied. Inhibition efficiency of benzimidazole derivatives was increased by inhibitor concentration. The data revealed that 2ABI showed better corrosion inhibition performance due to its chemical structure.

The effect of phosphoric acid surface treatment (containing 2ABI (0.05M) as a corrosion inhibitor) on the adhesion, corrosion performance and cathodic delamination resistance of the epoxy powder coating was assessed. It was observed that phosphoric acid washing process enhanced the adhesion bonds in the organic coating/steel interface leading to the increase of adhesion strength of the coating system. This could be attributed to the formation of a protective anti corrosive layer consisting of $Fe_3(PO_4)_2$ and $FePO_4$. The EIS results showed that the anticorrosive performance of the epoxy powder coatings on the phosphoric acid washed mild steel was higher compared to the bare mild steel. Phosphoric acid makes a polar anti corrosive layer on the mild steel and enhances the adhesion of coating/substrate interface. This results in the improvement of corrosion resistance parameters. The cathodic disbondment resistance of the coating systems increased after acid washing process due to stronger adhesion bonds in the coating/substrate interface.

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