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Effect of 1 *H*-Benzimidazole Derivatives on Zinc by Treatments with Sodium Phosphate and Silicate in 0.5 M NaCl solution

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Abstract

Objectives: In this study, the inhibitory effect of 1*H*-benzimidazole, 2-methyl-1*H*-benzimidazole and 5-nitrobenzimidazole on zinc have been investigated. **Method**: For this purpose, we used current-potential and Electrochemical Impedance Spectroscopy (EIS) methods in 0.5M NaCl solution at 25°C. Zinc polished with sand paper, etched 20 minute in 0.15 M HCl solution, cleaned with distilled water immersed for pre-treatment with sodium hydrogen phosphate ($Na_2HPO_4.12H_2O$, pH 5.7) and sodium silicate (Na_2SiO_2) solution. **Findings**: Pre-treated coatings on the zinc increased inhibition effects of BIM derivatives. Inhibition efficiency was approximately 98%, for 1*H*-benzimidazole and 5-nitrobenzimidazole.

Keywords: Coatings, Corrosion, Organic Inhibitors, Phosphate, Silicate

1. Introduction

Zinc, a very active metal, corrodes quickly in aqueous solutions[1]. There is adequate evidence that phosphates are widely used for surface treatment of zinc and galvanized steel[2-4]. Sodium phosphate, environmentally acceptable for surface treatment, was an effective inhibitor for zinc corrosion in aerated 0.5M NaCl[5]. Benzimidazole and its derivatives were effective inhibitors, particularly for zinc[6]. Corrosion inhibition efficiency of benzimidazoles is same as other heterocyclic compounds[7]. Organic inhibitor, by metal surface adsorption was effective against corrosion[8-11]. Benzimidazole compounds contain nitrogen atom on the heterocyclic ring, showing two convenient sites for adsorption. Substitute groups such as methyl and nitro play an important role on the inhibition efficiency of compounds. The decreased corrosion resistance of the methyl group is due to the loss of an electron. These electrons donated to the aromatic ring, increases their negative charge strengthening the interaction with the zinc surface[12]. The adsorption of corrosion inhibitor depends mainly on physical-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density at the donor atoms, p-orbital character of donating electrons[13–17] and also on the electronic structure of the molecules[18,19].

The aim of the present study is to assess the effect of pre-treatment with sodium hydrogen phosphate ($Na_2HPO_4.12H_2O$) and sodium silicate (Na_2SiO_2) solu-

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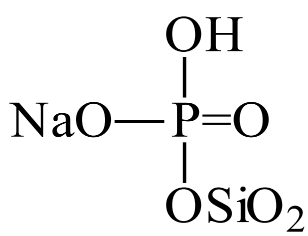
tion and the inhibiting effect of benzimidazole and derivatives on the zinc corrosion in NaCl solution. Also to obtain synergistic effect of phosphate and silicate effect on the inhibition of 1*H*-benzimidazole (BIM), 2-methyl-1*H*-benzimidazole (2-*M* BIM) and 5-nitrobenzimidazole (5-*N* BIM). The literature does not mention about the synergistic effect of sodium phosphate and sodium silicate. In order to obtain a steady state metal surface electrode samples immersed motionlessly in 0.15M HCl solution for 20 seconds, before pre-treatment. Disodium hydrogen phosphate and disodium silicate react to form a phospho-silicate compound with zinc ion[20].



(Sodium phospho-silicate bond)

Due to electron-withdrawing, substituent–NO_2 group on the aromatic ring increased hydrogen atoms, which acts on the pyridine type nitrogen atom as an inductive[6] and H^+ react to form with a Lewis base group SiO_2^{-2} ion.

2. Experimental Method

2.1 Materials

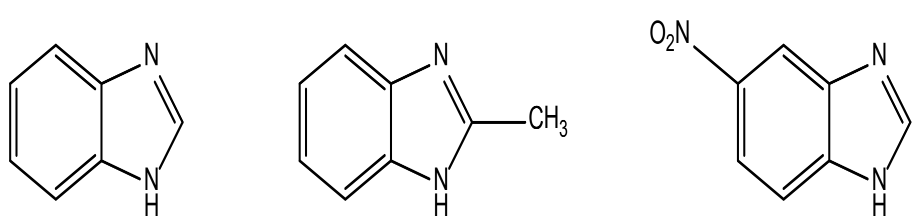
Working electrode was prepared by a cylinder high pure zinc rod, (Aldrich 99.999 % purity, 2mm diameter). It fixed in the Teflon tube with adhesive. The reference electrode adjusted near working electrode surface for balancing the drop in ohm. All chemicals used in this study were of Merck analytical grade. Double-distilled water used in the preparation all of the solutions.

2.2 Procedure

The working electrode polished with emery papers with 1200 grit and etched in 0.15 M HCl solution for 20 seconds before the experiments to form a steady-state surface. The frequency range at the AC-impedance spectroscopy was 10^{+5}-0.1Hz and the potential range for Tafel extrapolation method was ±0.3V corrosion potential. All experiments carried out at 25°C. The inhibition efficiency of zinc calculated from the following equation (Eq.1,2),

$$IE(\%) = \left(1 - i_{cor}/i^{0}_{cor}\right) \times 100 \quad (1)$$

$$IE(\%) = \left(1 - R^{0}_{p}/R_{p}\right) \times 100 \quad (2)$$



BIM   2-CH_3 BIM   5-NO_2 BIM

Figure 1. Structure of 1*H*-benzimidazole (BIM) and its derivatives.

$$i_{corr} = \frac{\beta_a . \beta_c}{2{,}303(\beta_a + \beta_c)} \bullet \frac{\Delta I}{\Delta E} = \frac{\beta_a . \beta_c}{2{,}303(\beta a + \beta c)} \bullet \frac{1}{R_p} = \frac{B}{R_p} \quad (3)$$

Here, i_{corr} and i^0_{cor} are showed the corrosion current densities and R^0_p and R_P polarization resistance in uninhibited and inhibited solutions respectively. Corrosion rate, polarization resistance and other corrosion characteristics of coated zinc carried out in 1 M NaCl + 10^{-3} M M organics solutions. Corrosion rates were also calculated using Stern- Geary equation (Eq.3). All chemicals used were of Merck grade. Corrosive media were prepared with double distilled water. All measurements carried out in aerated solution at 25°C. Zinc electrode converted by immersion 20 minutes in 0.1M Na_2HPO_4 and 20 seconds in Na_2SiO_2 solutions respectively. Working electrode for obtaining better electrode surface immersed 20 seconds in 0.15M HCl solution before immersion in the conversion coating solutions, washed with double distilled water at every pre-treated step.

2.3 Apparatus

Open circuit potentials, recorded 20 minutes time. Current-potential curves were obtained in studied solutions by scan rates of 1mV/s. AC impedance curves were performed by using CH Instruments 660B Potentiostat, Electrochemical Work Station of computer programme, BAS disc electrode, Poly Science model 9106 thermostat system, saturated Ag/AgCl reference and platinum wire as counter electrode.

2.4 Experimental

Purity of 99.999 % zinc specimen (2mm diameter) used to form working electrode. The metal surface polished with emery paper of grade 1200. Subsequently the electrode immersed into the 0.15 M HCl solution for 20 mins, immersed into conversion coating solutions (phosphate or silicate) and placed in the electrochemical cell. Working electrode at each step washed with double distilled water.

2.5 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy performed using CH Instruments 660 B potentiostat Workstation and BAS Rotating Disc Electrode (RD-2). Impedance was measured a frequency range 0.1 Hz to 100 kHz, and amplitude is 5mV/s. All experiments carried out after dipping 20 min to the studied solution. Double layer capacitance calculated at the impedance curves using equation:

$$C_{dl} = \frac{1}{2\pi f (Z_{im(\max)}) R_p} \quad (4)$$

where, C_{dl} and f are showed the double layer capacitance and frequency when the imaginary component of impedance (Z_{im}) was maximum.

3. Results and Discussion

The corrosion current density was determined by extrapolating anodic and cathodic Tafel lines to the corrosion potential. Inhibition efficiency of organics IE(%), was calculated from equation 1. At the corrosion of zinc oxidation as anodic and oxygen reduction occurs.

$$Zn \rightarrow Zn^{+2} + 2e^-$$

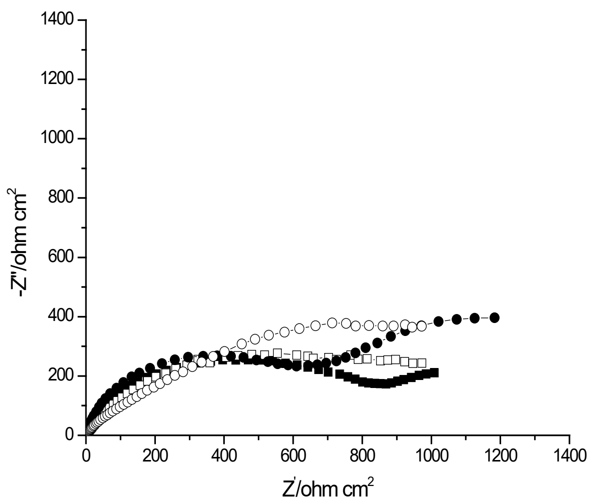
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

Solubility of zinc hydroxide is low in neutral medium. For this reason, $[Zn(OH)_2]$ precipitates and subsequently zinc oxide, (ZnO) forms at the zinc surface.

$$Zn^{+2} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

Table 1. Analitical and physical data of BIM and its derivatives

Compound	Formula	Molecular mass(g mol^{-1})	Melting point (°C)	Solvent
1-*H* BIM	$C_7H_6N_2$	118.4	171-173	Ethanol-water
5-NO_2 BIM	$C_7H_5N_3O_2$	163.14	205-207	Ethanol-water
2-CH_3 BIM	$C_8H_8N_2$	132.17	175-177	Ethanol-water



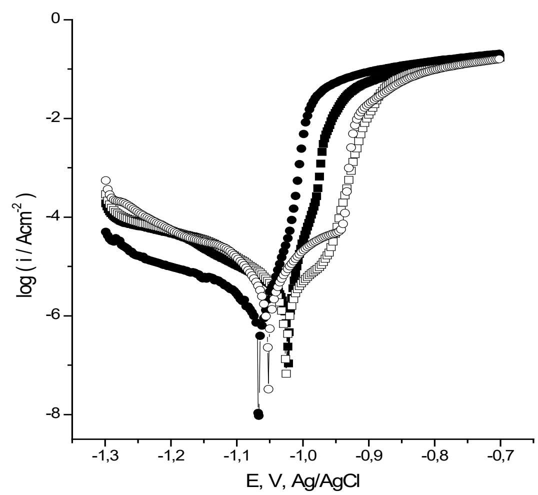
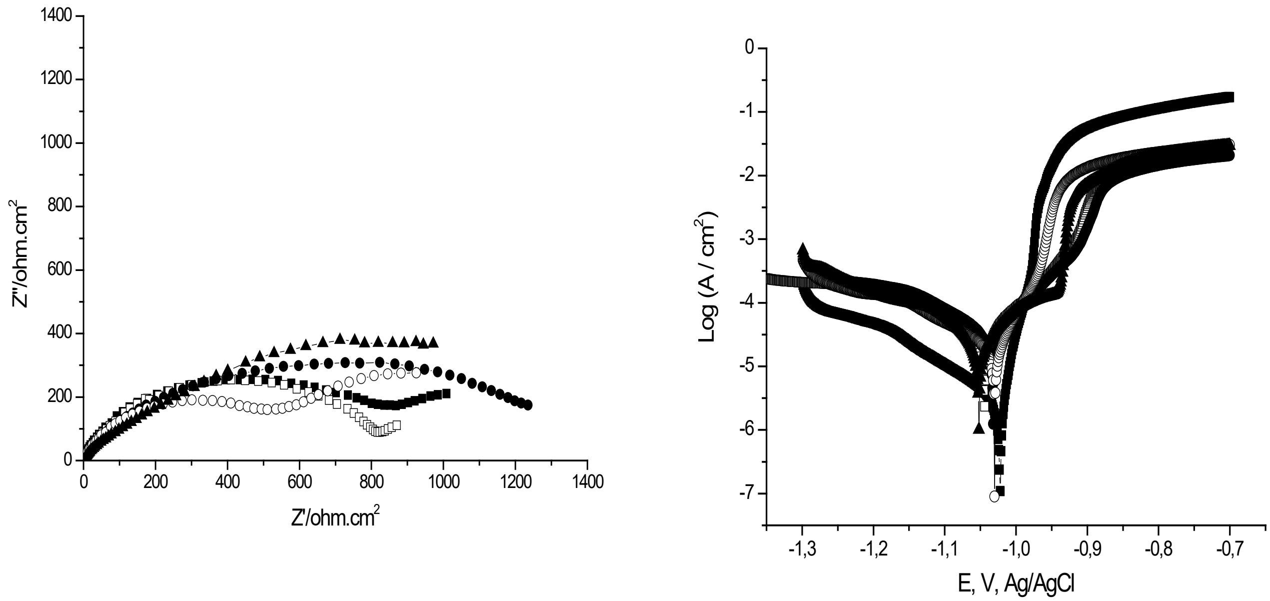


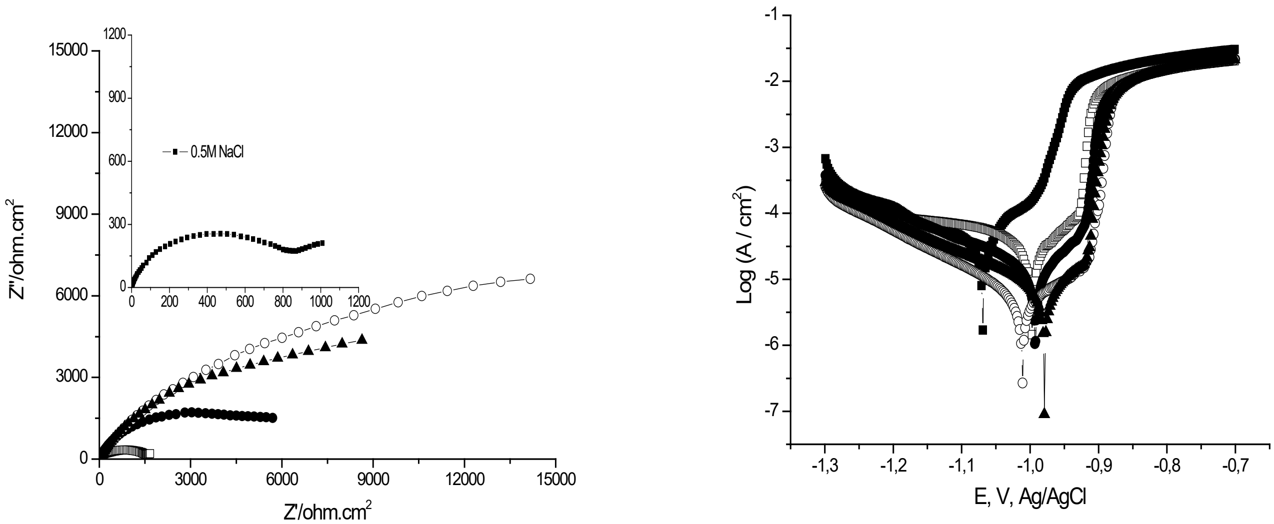
Figure 2. (a) AC-impedance. (b) current-potential curves for coated with phosphate or silicate zinc in 0.5M NaCl solution [■: uncoated □: Phosphate (20 min), ●:Silicate (20 s), ○: Phosphate (20 min) + Silicate (20 s)].

These compounds formed a passive film on the zinc surface[21]. In the presence of Cl^- , soluble Zn^{+2}-OH-Cl^- complexes form an effective passive film on the metal surface[22]. If the zinc surface coated with phosphate or silicate, the negative electrode potential shift with inhibition occurs in the studied solution. Adsorption BIM and derivatives on metal surface formed on the N atom. Electrode potentials shifted to a slightly more positive direction with the adsorption of organics. This shows that organics act as anodic inhibitor on the corrosion of zinc in the studied solution. Functional groups play an important role on the charge density of N atoms on the imidazole ring, and this role changed the efficiency of the inhibitor. This effect increased inhibitory activity and decreased double-layer capacity. BIM and its derivatives have physical and analytical properties given in Table 1. Corrosion parameters of pure zinc pretreated with phosphate (pH 5.7) 20 min and silicate 20 sec in 0.5 M NaCl solution containing 10^{-3} M BIM, 5(6)-N BIM and 2-M BIM at 25°C given in Table 2.



(a) (b)

Figure 3. . (a) AC-impedance. (b) current-potential curves for coated with phosphate or silicate zinc in 0.5M NaCl + 10-3 M 2-CH3 BIM solution [□: uncoated, ●:Phosphate (20 min), ○: Silicate(20sec), ▲: Phosphate (20 min) +Silicate(20sec)].



(a) (b)

Figure 4. .(a) AC-impedance. (b) current-potential curves for coated with phosphate or silicate zinc 0.5M NaCl + 10-3 M BIM solution [□: uncoated, ●:Phosphate (20 min), ○: Silicate(20sec), ▲: Phosphate (20 min) +Silicate(20sec)].

Table 2. Corrosion parameters of zinc % 99.999 purity for pre-treated with phosphate (pH 5.7) 20 min and silicate 20 sec in 0.5 M NaCl solution containing 10-3 M BIM, 5(6)-NBIM and 2MBIM at 25°C

Inhibitor $c=10^{-3}$ M	E_{corr} (V)	$-b_c$ (mVdec^{-1})	b_a (mVdec^{-1})	i_{corr} μAcm^{-2} (i_{corr} Stern-Geary)	R_p (ohm. cm^2)	i_{corr} *Stern-Geary*	C_{dl} ($\times10^{-10}$ F/cm^2)	*IE* (%)
Blank	-1.024	161	306	13.0	3300	12.5	12.8	-
Silicate	-1.032	193	62	3.0	6276	3.30	2.62	77
Phosphate	-1.032	184	36.0	2.0	6447	2.00	2.55	85
Phosphate+ Silicate	-1.117	170	48	4.5	5060	3.20	3.25	65
BIM	-1.055	338	30	3.44	8875	3.50	3.20	74
Phosphate	-0.990	173	25	0.76	12200	0.77	1.35	94
Silicate	-1.005	132	20	0.14	55500	0.13	2.96	98
Phosphate+ Silicate	-0.950	130	36	0.44	25436	0.48	6.47	96
2-M BIM	-1.004	232	38	3.90	3760	3.80	4.40	71
Phosphate	-1.042	232	38.5	3.92	3758	3.82	4.40	71
Silikate	-1.034	207	50	4.10	5850	3.00	4.30	70
Phosphate+ Silicate	-1.060	196	48.5	2.81	4110	4.10	4.00	45
5-N BIM	-0.940	654	167	361	175	330	94.0	-
Phosphate	-0.914	200	140	13.6	700	51.0	23.5	-
Silicate	-0.971	284	107	4.86	6970	4.84	2.36	64
Phosphate+ Silicate	-0.990	151	19	0.26	27700	0.27	0.60	98

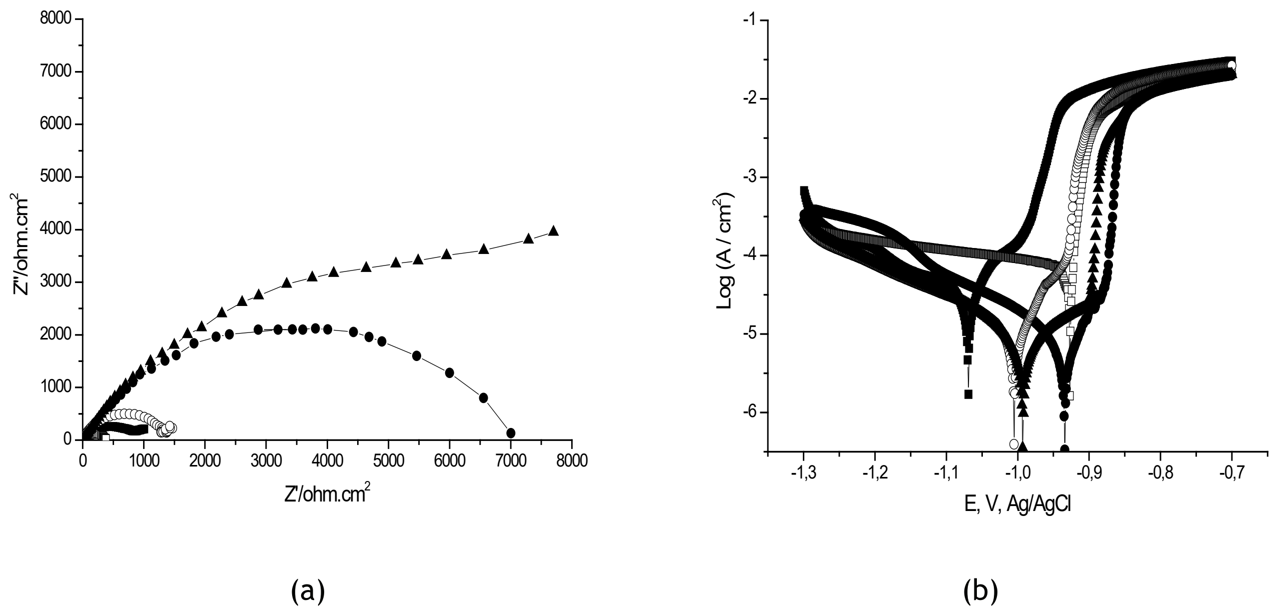


Figure 5. (a) AC-impedance . (b) current-potential curves for coated with phosphate or silicate zinc 0.5M NaCl + 10-3 M 5-NO2BIM solution [□: uncoated, ●: Phosphate (20 min), ○: Silicate (20sec), ▲: Phosphate (20 min) +Silicate (20sec)]

4. Conclusion

-The inhibitory effect of mixture phosphate and silicate was better with additive BIM (96 %) and 5-NBIM (98 %); the inhibitive efficiency was over 95 per cent the 10^{-3}M concentration of inhibitor, reaching a maximum of 98 percent.

-The inhibitory effect of BIM and 5-NBIM was better after pre-treatment mixture phosphate and silicate; inhibitive efficiency was over 95 percent at 10^{-3}M concentration of derivatives.

-The electrode potential shifted to the negative direction, and decreased inhibition with phosphate and silicate surface coating.

- Phosphate and disodium silicate provide a synergistic improvement presence of BIM and 5-nitro BIM in the 0.5M NaCl solution.

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