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Electrochemical and Surface Characterization Studies of New Triazole Derivatives on Mild Steel

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Corrosion inhibition by Zn^{2+}, 4-phosphonobutyric acid (4-PBA) and two new benzotriazole derivatives namely 1-(2-pyrrolecarbonyl)-benzotriazole and 1-(2-thienylcarbonyl)benzotriazole on mild steel in aqueous media has been investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. Further characterization using XRD and SEM demonstrates the adsorption of inhibitor and the formation of corrosion products on the mild steel surface, respectively. Combination of 1-(2-pyrrolecarbonyl)benzotriazole and 1-(2-thienylcarbonyl)benzotriazole along with Zn^{2+} and 4-phosphonobutyric acid shows better corrosion inhibition efficiency than other inhibitor combinations and the individual inhibitors.

Key Words: Mild steel, Benzotriazole, Corrosion, Potentiodynamic polarization, Inhibition.

INTRODUCTION

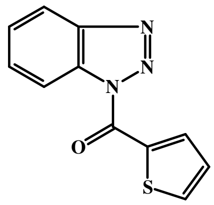
Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Before the 1960s, corrosion treatments of carbon steels in cooling water systems based on inorganic inhibitors such as chromates, nitrites, polyphosphates and zinc salts provided reliable corrosion protection. The use of chromates is now submitted to severe restrictions due to their high toxicity. Thus, the search for new and efficient corrosion inhibitors has become a necessity to secure metallic materials against corrosion. Over the years, considerable efforts have been deployed to find suitable compounds of organic origin to be used as corrosion inhibitors in various corrosive media, to either stop or delay to the maximum the attack of a metal[1-6]. Nitrogen-containing heterocyclic compounds are considered to be an effective corrosion inhibitors, for instance, benzotriazole has been used as an inhibitor for the corrosion of mild steel, copper and its alloys[7-9]. Many phosphonic acid derivatives and phosphonates have been used as inhibitors for stainless steel and iron[10,11]. In this paper, we report the corrosion behaviour of mild steel in ground water medium in the presence and absence of benzotriazole derivatives namely 1-(2-pyrrolecarbonyl)benzotriazole (PCBT) and 1-(2-thienylcarbonyl)benzotriazole (TCBT). Weight loss measurements, electrochemical techniques such as potentiodynamic polarization, electrochemical impedance and surface characterization techniques like XRD and SEM were also performed to study the corrosion behaviour of mild steel in ground water medium. The comparative study of benzotriazole derivatives with Zn^{2+} and phosphono derivatives indicates that the corrosion inhibition efficiency of 1-(2-pyrrolecarbonyl)benzotriazole and 1-(2-thienylcarbonyl)-benzotriazole along with Zn^{2+} and 4-phosphonobutyric acid offered good corrosion inhibition efficiency than other inhibitor combinations and the individual inhibitors.

EXPERIMENTAL

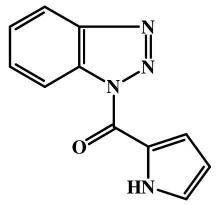
Synthesis of benzotriazole derivatives: Benzotriazole derivatives (TCBT and PCBT) were synthesized by adopting standard procedures[12-14] and the products were characterized by FT-IR and NMR. The structures of the compounds under investigation are given in Fig. 1.

Specimen preparation: Mild steel samples with the composition C-0.13 %, P-0.032 %, Si-0.014 %, S-0.025 %, Mn-0.48 % and balance Fe were used. For each electrochemical study, specimens of size 1 cm × 1 cm × 0.3 cm were cut, embedded in epoxy resin and mechanically polished with silicon carbide papers (from grades 120 to 1200) followed by then washing with double distilled water, degreasing with acetone and drying at room temperature.

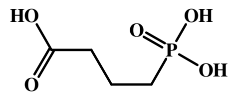
Weight loss measurements: Mild steel specimens in triplicate were immersed in ground water at room temperature for each inhibitor concentration for 7 days. The specimens were removed, rinsed in double distilled water and acetone



1-(2-Thienylcarbonyl)benzotriazole (TCBT)



1-(2-Pyrrolecarbonyl)benzotriazole (PCBT)



4-Phosphonobutyric acid (4-PBA)

Fig. 1. Structures and names of the benzotriazole derivatives and phosphonic acid derivative

then kept in a desiccator. Then the weight loss was determined in order to calculate the inhibition efficiency (IE) using the formula.

$$IE(\%) = \frac{W_o - W_i}{W_o} \times 100$$

where, W_o and W_i are the weight loss in the absence and presence of inhibitor respectively.

Electrochemical studies: All electrochemical measurements were performed using an electrochemical workstation (Model No: CHI 760, CH Instruments, USA) and all experiments were carried out at a constant temperature of 28 ± 2 ºC with ground water as electrolyte. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively and the working electrodes comprised the mild steel specimens of 1 cm^2 area. The tip of the reference electrode was positioned very close to the surface of working electrode by the use of a fine Luggin capillary in order to minimize ohmic potential drop. The remaining uncompensated resistance was reduced by using the electrochemical workstation.

Potentiodynamic polarization measurements: The potentiodynamic polarization studies were carried out at a scan rate of 0.01 mV s^{-1}. In all cases the OCP was established first and then the polarization measurements were carried out. The polarization curves for mild steel specimens in the test solution with and without various concentrations of inhibitor were recorded from 1200 to 0 mV.

Electrochemical impedance studies: Electrochemical impedance studies were carried out with the same setup used for potentiodynamic polarization studies. The applied ac perturbation signal was about 10 mV within the frequency range 100 kHz to 1 Hz.

Surface examinations: The nature of the film formed on the surface of the metal specimens was analyzed by various surface analytical techniques. After 7 days of immersion, the specimens were taken out and dried. The corrosion products on the surface of mild steel specimens exposed to ground water in the absence and presence of inhibitors were identified by XRD (model: Bruker D_8 Advance-Germany). The surface morphology of each specimen was also examined using scanning electron microscope (SEM, JEOL, Japan).

RESULTS AND DISCUSSION

Weight loss measurements: The corrosion rate and inhibition efficiency of all the studied inhibitors system was given in Table-1. There is a significant decrease in the corrosion rate with increase in concentration of each inhibitor and the extent of inhibition depends on the nature and concentration of the inhibitor. The optimum concentration was evaluated based on inhibition efficiency; for TCBT and PCBT, these are 16 and 12 ppm respectively. TCBT and PCBT have a maximum inhibition efficiency of 70.7 and 74.4 % respectively. Other individual inhibitors such as Zn^{2+} and 4-PBA showed a maximum inhibition efficiency of 67.7 and 68.3 % respectively while the binary combination PCBT + 4-PBA had a inhibition efficiency of 80.3 %. Among all the individual, binary and ternary systems studied by weight loss method the ternary combination of PCBT + Zn^{2+} + 4-PBA system had shown the maximum inhibition efficiency up to 91.0 % and the corrosion rate was found to be 0.59 mpy.

TABLE-1
WEIGHT LOSS MEASUREMENTS OF MILD STEEL IN GROUND WATER IN THE ABSENCE AND PRESENCE OF VARIOUS AND OPTIMUM CONCENTRATION OF SIMPLE, BINARY AND TERNARY MIXTURES OF BENZOTRIAZOLE, PHOSPHONO DERIVATIVES AND ZN^{2+} AT 30 ºC

Inhibitor	Inhibitor conc. (ppm)	Corrosion rate (mpy)	Inhibition efficiency (%)
Bank	-	6.6	-
TCBT	10	3.91	40.75
	12	3.31	49.84
	14	2.35	64.30
	16	1.91	70.71
	18	2.51	61.96
	20	2.95	55.30
	22	3.42	48.18
PCBT	6	3.71	43.78
	8	3.39	48.64
	10	3.10	53.00
	12	1.70	74.40
	14	2.19	66.80
	16	3.02	54.24
	18	3.68	44.24
4-PBA	4	3.61	45.30
	6	3.42	48.18
	8	2.90	56.06
	10	2.09	68.30
	12	2.95	55.30
	14	3.52	46.60
	16	3.85	41.66
Zn^{2+}	30	3.2	51.51
	45	2.95	55.30
	60	2.30	65.15
	75	2.1	67.70
	90	2.25	65.90
	105	2.51	61.96
	120	2.76	58.18
TCBT + Zn^{2+}	16 + 75	1.5	77.90
PCBT + Zn^{2+}	12 + 75	1.3	80.10
PCBT + 4-PBA	12 + 10	1.30	80.30
TCBT+Zn^{2+}+ 4-PBA	16 + 75 + 10	0.72	89.00
PCBT+ Zn^{2+}+ 4-PBA	12 + 75 + 10	0.59	91.00

Electrochemical measurements

Potentiodynamic polarization measurements: The potentiodynamic polarization parameters of mild steel immersed in ground water for all the inhibitor systems are given in Tables 2 and 3. The inhibition efficiency increases appreciably with increase in inhibitor concentration up to the optimum level, after which it decreases. The optimum concentrations were evaluated based on the inhibition efficiency and the combination of benzotriazole derivatives with Zn^{2+} and 4-PBA was also studied. The polarization curves obtained in the absence and presence of various inhibitors are shown in Figs. 2 and 3. Comparison of the curves shows that, with respect to the blank, increasing the concentration of the additive PCBT up to the optimum level gave a consistent decrease in both anodic and cathodic current densities. PCBT acts as a mixed-type inhibitor with predominant cathodic effect. All the studied benzotriazole derivatives along with zinc act as mixed-type inhibitors with cathodic predominance in nature. The presence of active sites such as aromatic rings and heteroatoms in the benzotriazole derivatives are responsible for the adsorption. Their corrosion inhibition efficiencies are directly proportional to the amount of adsorbed inhibitor. The corrosion potential shows a clear tendency to be more negative for all the individual inhibitors except 4-PBA for which the shift in the E_{corr} value is positive.

TABLE-2
POTENTIODYNAMIC POLARIZATION PARAMETERS OF MILD STEEL IN GROUND WATER CONTAINING VARIOUS CONCENTRATIONS OF SIMPLE INHIBITOR SYSTEM AND OPTIMUM CONCENTRATIONS OF BINARY AND TERNARY INHIBITORS SYSTEM

Inhibitor	Inhibitor concentration (ppm)	E_{corr} (mV)	i_{corr} (μA cm^{-2})	Corrosion rate (mpy)	Inhibition efficiency (%)
Blank	-	-640	12.59	6.0	-
	10	-795	7.41	3.5	41.1
	12	-744	6.12	2.9	51.4
	14	-740	4.38	2.1	65.2
TCBT	16	-775	3.55	1.7	71.8
	18	-760	4.74	2.2	62.4
	20	-725	5.60	2.6	55.5
	22	-745	6.49	3.1	48.5
	6	-715	7.08	3.3	43.8
	8	-785	6.30	3.0	50.0
	10	-715	5.82	2.7	53.8
PCBT	12	-720	3.09	1.5	75.5
	14	-748	4.16	2.0	66.9
	16	-770	5.71	2.7	54.6
	18	-774	6.96	3.3	44.7
	30	-655	6.02	2.8	52.2
	45	-690	5.62	2.7	55.4
	60	-750	4.26	2.0	66.2
Zn^{2+}	75	-705	3.98	1.9	68.4
	90	-740	4.16	2.0	66.9
	105	-740	4.78	2.3	62.0
	120	-690	5.25	2.5	58.3
	4	-712	6.82	3.11	45.8
	6	-744	6.38	2.91	49.3
	8	-686	5.39	2.46	57.2
4-PBA	10	-618	3.85	1.76	69.4
	12	-709	5.56	2.54	55.8
	14	-672	6.68	3.05	46.9
	16	764	7.28	3.32	42.2

TABLE-3
POTENTIODYNAMIC POLARIZATION PARAMETERS OF MILD STEEL IN GROUND WATER CONTAINING OPTIMUM CONCENTRATIONS OF BINARY AND TERNARY INHIBITORS SYSTEM

Inhibitor	Concen. (ppm)	E_{corr} (mV)	i_{corr} (μA cm^{-2})	Corrosion rate (mpy)	Inhibition efficiency (%)
Blank	-	-640	12.59	6.0	-
TCBT+Zn^{2+}	16 + 75	-740	2.88	1.4	77.1
PCBT+Zn^{2+}	12 + 75	-735	2.51	1.2	80.0
PCBT+4-PBA	12 + 10	-552	2.38	1.0	81.0
TCBT+Zn^{2+}+4-PBA	16+75+10	-736	1.34	0.6	89.3
PCBT+Zn^{2+}+4-PBA	12+75+10	-695	1.07	0.5	91.5

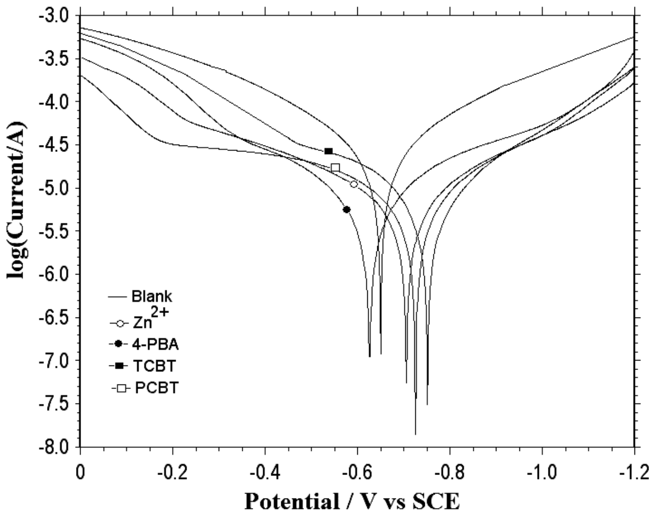


Fig. 2. Potentiodynamic polarization curves of mild steel in groundwater in the presence and absence of optimum concentration of Zn^{2+}, 4-PBA, TCBT and PCBT

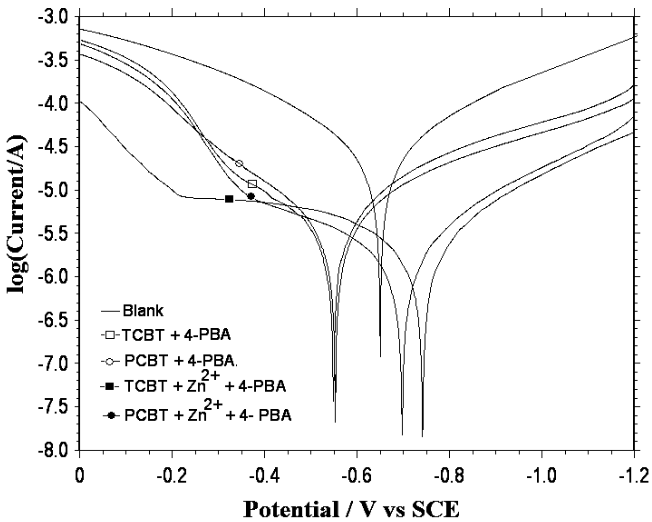


Fig. 3. Potentiodynamic polarization curves of mild steel in ground water in the presence and absence of optimum concentration of binary and ternary combinations of benzotriazole derivatives with Zn^{2+} and 4-PBA

With the aid of Tafel extrapolation the corrosion inhibition efficiencies of TCBT and PCBT were found to be 71.8, 75.5 % for optimum concentrations of 16 and 12 ppm respectively. Other individual inhibitors such as Zn^{2+} and 4-PBA showed maximum inhibition efficiencies of 68.4 and 69.4 %, respectively. In the presence of Zn^{2+} and 4-PBA, the efficiency of TCBT and PCBT is increased to 89.3 and 91.5 % respectively. Correlating the values obtained for individual inhibitors with that of the combinations, it is evident that the addition of Zn^{2+} and 4-PBA to the benzotriazole derivatives controls the cathodic and anodic reactions. Initially benzotriazole compounds are adsorbed on the metal surface and after the addition of 4-PBA, Fe(II)- phosphonate complex is formed as a protective layer which enhances the corrosion inhibition efficiency. This confirms that the combination of benzotriazole compounds, Zn^{2+} and 4-PBA provides enhanced corrosion inhibition.

Electrochemical impedance studies: Typical Nyquist plots obtained for mild steel immersed at open circuit potential for 1 h at the optimum inhibitor concentration are shown in Fig. 4 and the parameters obtained are shown in Table-4. From the impedance plots of the individual inhibitors (TCBT, PCBT, Zn^{2+} and 4-PBA), it is evident that the values of charge transfer resistance increase in the order TCBT < PCBT, when compared to the blank while the capacitance values decrease as TCBT > PCBT. This trend indicates that the inhibitors cover the surface of the metal due to adsorption thereby reducing the capacitive effects. For PCBT and Zn^{2+} combination further increase in the charge transfer resistance is noted and this value reaches a maximum for PCBT, Zn^{2+} and 4-PBA mixture (2.3605×10^4 Ω), demonstrating that this combination provides maximum corrosion protection. This fact is further substantiated from the decrease in double layer capacitance (1.72 μF) for PCBT, Zn^{2+} and 4-PBA mixture since lower values of double layer capacitance indicate thickening of the inhibitor film. All the AC measurements show the same trend as those observed from DC polarization.

Surface examination results

X-ray diffraction patterns: The XRD patterns of the corrosion products give qualitative information about the possible phases present. The patterns obtained clearly reveal the presence of metal and metal oxide phases. The XRD results are presented in Figs. 5a-c. The peak due to iron appears at 2θ = 43.8º, 60.1º and 74.5º. Peaks at 2θ = 30.4º, 35.9º and 62.5º

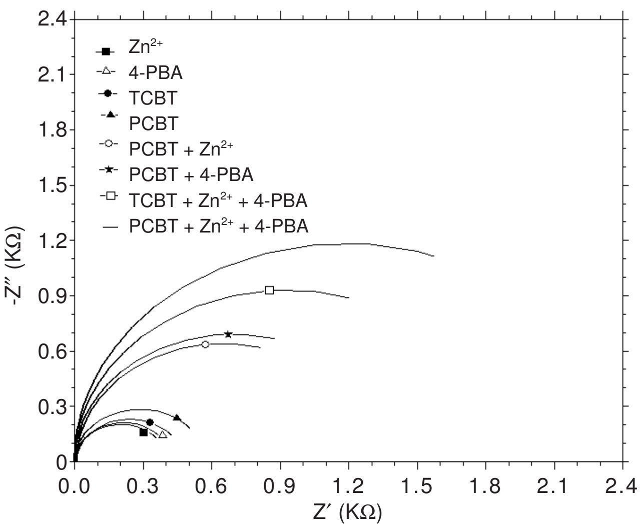


Fig. 4. Nyquist plots of mild steel in ground water in the presence and absence of optimum concentration of binary and ternary combinations of benzotriazole derivatives with Zn^{2+} and 4-PBA

TABLE-4
ELECTROCHEMICAL IMPEDANCE PARAMETERS OF MILD STEEL IN GROUND WATER WITH OPTIMUM CONCENTRATION OF SIMPLE AND TERNARY INHIBITORS SYSTEM

S. No.	Inhibitors	C_{dl} (μF)	$R_{ct} \times 10^4$ (Ω)
1	Blank	15.03	0.0130
2	TCBT	7.05	0.4606
3	PCBT	6.49	0.5685
4	Zn^{2+}	7.42	0.3981
5	4-PBA	7.24	0.4228
6	TCBT + Zn^{2+}	6.11	1.2589
7	PCBT + Zn^{2+}	5.81	1.2823
8	PCBT + 4-PBA	5.24	1.3810
9	TCBT + Zn^{2+}+ 4-PBA	2.31	1.8620
10	PCBT + Zn^{2+}+ 4-PBA	1.72	2.3605

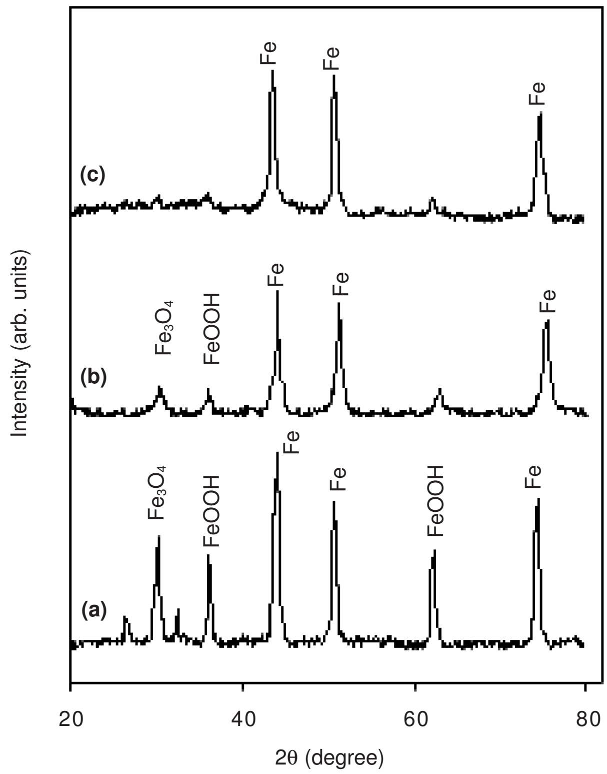


Fig. 5. XRD pattern of (a) blank, (b) PCBT + 4-PBA and (c) PCBT + Zn^{2+} + 4-PBA

can be assigned to oxides of iron. Thus, the surface of the metal immersed in ground water contains Fe_3O_4 and FeOOH. The XRD pattern for the metal immersed in the ground water containing optimum concentration of PCBT + Zn^{2+} + 4-PBA is given in Fig. 5c. The intensity of the peaks due to oxides of iron, such as Fe_3O_4 and FeOOH, are found to be very low and the peaks due to iron alone observed at 2θ = 43.7º, 50.9º and 74.3º are very high.

SEM results: Fig. 6 shows the scanning electron micrograph of mild steel exposed to ground water in the absence and presence of optimum concentration of the inhibitors. The SEM micrograph (Fig. 6a) shows that the surface is highly damaged in the absence of the inhibitor and the flakes are seen which show corrosion products like metal hydroxides and its oxides. While Fig. 6b and c shows the SEM micrographs of mild steel specimens exposed to the mixtures of PCBT +

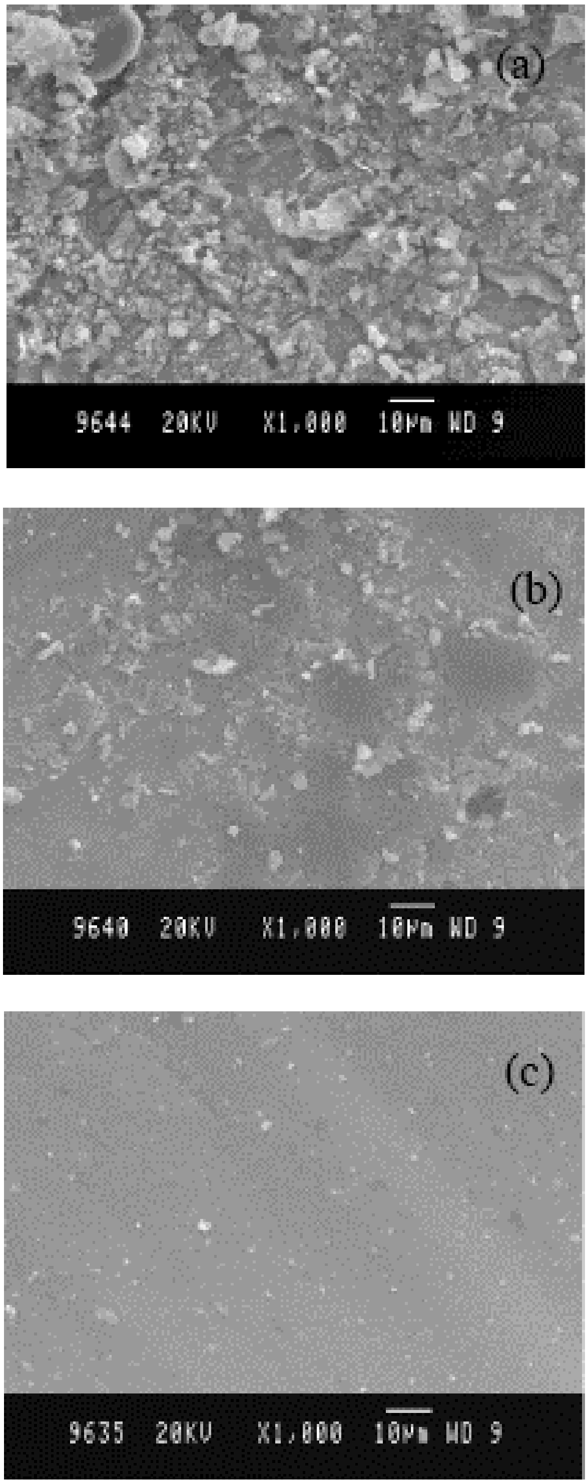


Fig. 6. SEM micrographs of (a) blank (b) presence of PCBT + 4-PBA and (c) presence of PCBT + Zn^{2+} + 4-PBA

4-PBA and PCBT + Zn^{2+} + 4-PBA, it can be seen that the metal surface is fully covered with the inhibitor molecules leading to a high degree of protection against corrosion. These observations clearly prove that the inhibition is due to the formation of stable film through the process of adsorption of the organic molecules on the metal surface.

Conclusion

- The synthesized benzotriazole derivatives PCBT and TCBT were found to suppress both anodic and cathodic reactions and hence behave as mixed type inhibitor.
- PCBT + Zn^{2+} + 4-PBA formulation shows the highest inhibition efficiency.
- The obtained results from weight loss measurements and electrochemical results are in good agreement.
- Surface analysis reveals the presence of an adsorbed film of benzotriazole derivative and Fe(II)-phosphonate complex on the mild steel immersed in PCBT + Zn^{2+} + 4-PBA system.
- The film formed at optimum concentrations of PCBT + Zn^{2+} + 4-PBA is more protective in nature rather than other combinations. This result is evident from the pictures of scanning electron micrographs for mild steel surface under various conditions.

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