

## *Chapter 6*

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## CHAPTER-6

# COMPARISON OF CORROSION INHIBITION PERFORMANCE OF SOME SELECTED BENZODIAZEPINES FOR MILD STEEL, COPPER AND ALUMINIUM

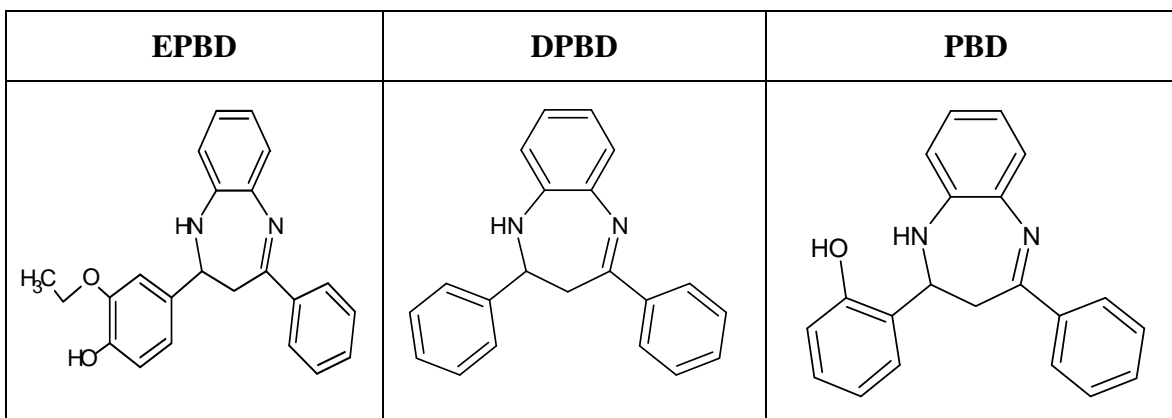
### 6.1 Introduction

There are numerous reports available on the corrosion of mild steel and inhibition by large number of organic compounds. Comparatively lesser works have been reported on the corrosion inhibition of copper and aluminium. Copper is used in electrical works for production of wires, sheets, tubes and alloys. Due to excellent thermal conductivity and good mechanical workability copper is commonly used in heating and cooling systems. It is resistant towards the influence of atmosphere and many chemicals. However in aggressive media it is susceptible to corrosion and no protective layer is formed <sup>1</sup>. Aluminium is the second most widely used metal after iron. It is used as anodic material for power sources with high energy densities. Aluminium forms protective films which are stable in aqueous medium in the pH range 4.5-8.5 but not stable in strong acid and alkaline solutions <sup>2</sup>.

Chapter 4 and 5 dealt with the study of corrosion inhibition properties of synthesized benzodiazepines, benzothiazepines and benzoxazepines for mild steel in 1M H<sub>2</sub>SO<sub>4</sub>. They were found to be excellent inhibitors. The relative performance of the compounds have been discussed in light of adsorption which in turn depended on substituents, heteroatoms, geometry and orientation of the molecule over the steel surface.

The purpose of this chapter is to assess the inhibition efficiency of three selected benzodiazepines for the corrosion of copper and aluminium and to make a comparison with that of mild steel. One Molar sulphuric acid was used as the corrosion medium. Inhibition efficiency was calculated by weight loss, polarization and impedance measurements. Surface morphology of the corroded and inhibited metals was analyzed using SEM and AFM techniques.

The compounds chosen are,



## 6.2 Results and Discussion

### 6.2.1 Weight loss measurements

The values of percentage inhibition efficiency (IE %) and corrosion rate obtained from weight loss method at different concentrations of each inhibitor for copper and aluminium are given in Tables 6.1 and 6.2. The corresponding data for mild steel are also presented in Table 6.3 for comparison of the results. Aluminium is more resistant to corrosion in 1M H<sub>2</sub>SO<sub>4</sub> than copper or iron as is evident from the corrosion rates in blank acid. Corrosion rate was found to be 17466 mpy for mild steel, 2170 mpy for copper and 1973 mpy for aluminium. This is because iron is more reactive than copper as per the standard potential series. As the concentration of each of the inhibitors is increased, the corrosion rate decreased or the inhibition efficiency increased. The maximum inhibition efficiency for each compound was obtained at 200 ppm and further increase in concentration did not cause any appreciable change in performance of the inhibitors. Analysis of the results showed that benzodiazepines are good inhibitors for copper and mild steel giving (> 90 % IE) and less effective for aluminium (60-75% efficiency at 200 ppm). With mild steel and copper 70% of protective action is observed even at lower concentrations and further increase brings about 95% protection (for EPBTZ and EPBD). The excellent inhibition effect may be attributed to the formation of a barrier film due to adsorption of the inhibitors on the metal surface involving interactions between lone pair of electrons on heteroatoms,  $\pi$ -electrons of aromatic rings with the metal atoms on the surface.

The influence of temperature on the corrosion behavior of mild steel, copper and aluminium and the inhibition by benzodiazepines have been studied by weight loss measurements in the temperature range 303-333K. The data are recorded in Table 6.4 – 6.6. As the temperature increased, the corrosion rate increased, with mild steel corroding at a much faster rate compared to copper or aluminium. Correspondingly the IE % decreased. The efficiency of EPBD for example is 68% and 60% for mild steel and copper respectively and 42% for aluminium at 333K. This may be due to the greater solubility of the adsorbed inhibitor and the passive oxide film on the aluminium surface in acid medium at the higher temperature.

The activation energies for the corrosion process have been calculated from the slope of the Arrhenius plots - log corrosion rate vs. reciprocal of absolute temperature (Figure 6.1-6.3). It is seen that the value of activation energy  $E_a$  for the corrosion of metals in 1M  $H_2SO_4$  in the presence of inhibitor is higher than in the absence of inhibitor. The inhibitors increase the energy of activation by decreasing the surface area available for corrosion and slow down the corrosion. The increased  $E_a$  may be attributed to the physical adsorption of the inhibitor<sup>3</sup>. A decrease in inhibition efficiency with increase in temperature might be due to the weakening of the physical adsorption leading to desorption of the adsorbed layer thereby exposing the surface to acid attack<sup>4</sup>.

The change in activation enthalpy  $\Delta H^*$ , the change in free energy  $\Delta G^*$  and change in entropy  $\Delta S^*$  can be calculated from the activation energy and using the thermodynamic relations as calculated in previous chapters.

$$\Delta H^* = E_a - RT$$

$$r = \frac{kT}{h} - e^{\frac{-\Delta G^*}{RT}} \quad \text{and}$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

Where T= 303 K. The values are recorded in Table 6.7-6.9

A comparison of the activation parameters corresponding to the uninhibited (blank acid) and inhibited systems for all the three metals indicate that the enthalpy value is more in the presence of inhibitors, since enthalpy is more for slower reactions, presence

of inhibitors reduces the rate of corrosion. Higher rate is usually associated with lower activation enthalpy and lower rate is associated with higher activation enthalpy<sup>5</sup>.

The  $E_a$  and  $\Delta H^*$  values are higher for copper than for mild steel or aluminium both in the presence and absence of inhibitors which indicates that copper is more resistant to corrosion. The negative  $\Delta G^*$  values suggest the spontaneous adsorption and inhibition of the inhibitor. The values for all the three metals are in the range -20 kJ/mol to -30 kJ/mol which reveals that the mechanism of inhibition is same for all the three metals which involves electrostatic interaction. The change in entropy of activation  $\Delta S^*$  is positive and the values are higher for the inhibited system which indicates that there is an increase in disorder during inhibition process, due to adsorption of the inhibitor from the solution and desorption of water molecules from the surface.

### Adsorption isotherm

The extent of corrosion inhibition by an organic compound depends on the surface conditions and the mode of adsorption of the inhibitor. The interaction between the inhibitor and the metal surface can be examined by adsorption isotherms, which give a relationship between degree of surface coverage and bulk concentration at a given temperature. The degree of surface coverage values  $\theta$  obtained from weight loss method with different concentrations of the inhibitors in 1M  $H_2SO_4$  at 303K for mild steel, copper and aluminium were tested with several adsorption isotherms. The best fit was obtained with Langmuir isotherm which is given as

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

The plot of  $C/\theta$  vs.  $C$  yields straight line (Figure 6.4-6.6) with regression coefficient  $R^2 = 0.99$ . The  $K_{ads}$  values can be calculated from the line intercept on  $C/\theta$  axis and is related to standard free energy of adsorption as,

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5 K_{ads})$$

The values of  $K_{ads}$ ,  $R^2$  and  $\Delta G^{\circ}_{ads}$  are tabulated (Table 6.10-6.12).  $R^2$  values are close to unity (0.99) showing that the adsorption of the selected benzodiazepines on copper, aluminium and mild steel are in conformity to Langmuir adsorption.  $K_{ads}$  values are high

showing stronger adsorption. The values are higher for copper indicating stronger adsorption of the compounds on copper surface than that of mild steel or aluminium.  $\Delta G_{\text{ads}}^{\circ}$  values are negative and greater than 30 kJ/mol and approach 40 kJ/mol, which is the threshold value for chemisorption mode. It may be attributed to the mixed mode of adsorption of the inhibitors (involving both physisorption and chemisorption).

### 6.2.2 Electrochemical AC impedance measurements

Corrosion behavior of mild steel, copper and aluminum in 1M H<sub>2</sub>SO<sub>4</sub> with different concentrations of the three benzodiazepines after immersion for 30 minutes was investigated by EIS at 303K. Nyquist plots displayed in Figure 6.7-6.9 for copper, Figure 6.10-6.12 for aluminium and Figure 6.13-6.15 for mild steel which revealed semicircles for all systems over the studied frequency range.

In the Nyquist plots for aluminium, small distortions were observed which may be attributed to surface roughness arising from impurities, dislocation, grain boundaries or due to the formation of porous layers of adsorbed inhibitors <sup>6</sup>.

In the Nyquist plots, the high frequency intercept with real axis  $Z'$  is assigned to the solution resistance  $R_s$  and low frequency with real axis is assigned  $R_t + R_s$ . The impedance spectra were analyzed by fitting the data to the equivalent circuit model as explained in chapter 4. The corresponding impedance parameters are presented in Table 6.13- 6.15. From the results it can be stated that the presence of the benzodiazepines increases the  $R_t$  values with corresponding decrease in  $C_{dl}$  values, which is attributed to the adsorption of the compounds on the metal by displacing water molecules to form a protective layer whose thickness increases with concentration. Maximum reduction in  $C_{dl}$  was observed for EPBD for all the three metals indicating its excellent inhibition efficiency.

### 6.2.3 Polarization measurements

The current-potential relationships for mild steel, copper and aluminium specimens in 1M H<sub>2</sub>SO<sub>4</sub> containing various concentrations of benzodiazepines are shown in Figure 6.16-6.24. The electrochemical data obtained from the polarization curves are given in Tables 6.16-6.18. Addition of benzodiazepines is seen to affect the cathodic partial reactions mostly, thereby reducing the cathodic current densities, for copper and

mild steel. Hence the compounds function as cathodic inhibitors. At higher concentrations they also reduce current density in the anodic domain and behave as mixed inhibitors. For aluminium, addition of the benzodiazepines reduces the anodic current densities (Figure 6.16-6.24) indicating that they function slightly as anodic inhibitors. The open circuit potentials for mild steel, copper and aluminium are -480 mV, +40 mV and -650 mV respectively. Polarization measurements were made in the range -200 mV to +200 mV with respect to the corresponding OCP. Analysis of polarization curves of aluminium reveals that the potential range in Tafel plots is short. A typical Tafel plot consists of three regions-Tafel region, plateau region and high polarization region. Eddy *et al.*, explained the difference of Tafel plots of aluminium as due to the dominance of Tafel region leading to a short potential range <sup>7</sup>.

The electrochemical parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), cathodic and anodic Tafel plots ( $b_c$ ,  $b_a$ ) obtained from polarization curves and the corresponding inhibition efficiency values (IE %) at different concentrations of EPBD, DPBD and PBD are recorded in Table 6.16-6.18. The corrosion current densities were determined by the extrapolation of the Tafel plots to the respective corrosion potential. It can be noted that the corrosion current density was more significantly reduced in the presence of EPBD, from the blank acid value of  $414 \mu\text{A cm}^{-2}$  for mild steel to  $53 \mu\text{A cm}^{-2}$ ;  $410 \mu\text{A cm}^{-2}$  for copper to  $122 \mu\text{A cm}^{-2}$ ,  $552 \mu\text{A cm}^{-2}$  for aluminium to  $230 \mu\text{A cm}^{-2}$  at 200 ppm concentration. The best efficiency was obtained for EPBD at this concentration. The shift of  $E_{\text{corr}}$  value is not much (5-10 mV for copper, 10-20 mV for mild steel and aluminium) suggesting that the compounds are mixed type.  $b_a$  and  $b_c$  values are both affected by the addition of inhibitors, but  $b_a$  the anodic Tafel slope is decreased much for aluminium which confirms that the benzodiazepines are mixed type but slightly anodic for aluminium.

#### 6.2.4 Scanning electron microscope (SEM)

Figure 6.25-6.27 (a-c) show the SEM micrographs of polished, corroded and inhibited copper, aluminum and mild steel respectively. Figure 6.27b show the severe corrosion attack of the metals in 1M  $\text{H}_2\text{SO}_4$ . Copper undergoes passivation and depassivation of the oxide film. A network of crack with dissolution of oxide film is seen on the surface

of the metals. In the presence of DPBD, the corrosion is reduced and a layer of adsorbed inhibitor molecules can be seen. The EDX spectrum of the inhibited coupons (Figure 6.28b, 6.29b and 6.30b) show a peak for nitrogen confirming the adsorption of the benzodiazepine. The data are presented in Table 6.19-6.21.

### **6.2.5 Atomic force microscope (AFM)**

Figure 6.31-6.33 (a-c) shows representative 3D AFM images of polished metal specimens and specimens after immersion in 1M H<sub>2</sub>SO<sub>4</sub> without and with 200 ppm of benzodiazepine DPBD. The corrosion products are seen clearly on the specimen immersed in blank acid. The presence of inhibitor is shown by the increased height of the scale bar in 6.31c-6.33c. The average roughness S<sub>a</sub>, root mean square roughness S<sub>q</sub> and the maximum peak to valley (P-V) height are tabulated in Table 6.22 to 6.24. Analysis of the values in the table shows that mild steel surface is heavily corroded when compared to copper and aluminium. The surface roughness S<sub>a</sub> values are 83.98, 104.84 and 160.65nm for the uninhibited metal surface. The average roughness values are considerably reduced to 42.08, 68.05 and 107.57.

### **6.3 Comparison of corrosion inhibition performance of benzodiazepines for mild steel, copper and aluminium.**

The inhibitive action of organic compounds is mainly due to their adsorption on the corroding metal. Adsorption is affected by the nature of surface charge on the corroded metal and by the molecular structure of the adsorbed organic compound. Surface charge of the metal is due to the electric field which arises at the interface when the metal is immersed in an electrolyte<sup>8</sup>. Potential of zero charge (PZC) is defined as the metal potential measured against a reference electrode under the conditions of zero charge on the metal. At the PZC, the ionic double layer is absent at the electrode and the electrode is able to adsorb the substance dissolved in the electrolyte. In the presence of a potential difference at the ionic double layer, the ability of the metal to adsorb the molecule will be reduced. Antropov proposed a special scale of potential ( $\phi$ ), and is given as,

$$\phi = OCP - PZC$$



When  $\phi > 0$ , the metal will be positively charged in this case anions will be adsorbed on the metal surface. When  $\phi < 0$ , the metal will be negatively charged and cations will be attracted from the solution <sup>9</sup>. Hence it is important to measure the value PZC in the presence and absence of inhibitors for the metal. Double layer capacitance is measured at various applied potentials. Figure 6.34-6.36 shows the variation of capacitance  $C_{dl}$  with potential measured in blank acid and in presence of 200 ppm of the inhibitor. The graph is V-shaped and the minimum in each curve is taken as PZC. Table 6.25 lists the values of OCP, PZC and  $\phi$  for copper, mild steel and aluminum measured with respect to SCE. PZC value of copper was found to be -0.30V in 1M H<sub>2</sub>SO<sub>4</sub>. This is in accordance with Ma *et al.*,<sup>10</sup> who have reported a value of -0.56 V in 0.5 mol/ L H<sub>2</sub>SO<sub>4</sub>. PZC of aluminium is close to the OCP which agrees with that reported in the literature <sup>11</sup>. For mild steel PZC occurs at -0.5 V which is also close to the OCP of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>. The excess charges of all the three metals are positive. Hence anions (sulphate ions) will get adsorbed first and the protonated inhibitor molecules get electrostatically bound with the adsorbed SO<sub>4</sub><sup>2-</sup> ions and prevent the metal dissolution <sup>12</sup>. In the presence of 200 ppm DPBD, the excess surface charge increases for mild steel and aluminium confirming the adsorption of the protonated benzodiazepine (DPBD) cation. The positive charge is more in the case of copper which show the stronger adsorption and inhibition of the protonated DPBD via adsorbed SO<sub>4</sub><sup>2-</sup> ions. The value is least for aluminum correspondingly the adsorption and inhibition efficiency are lesser.

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*Tables*

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**Table 6.1** Inhibition efficiencies of various concentrations of benzodiazepines for corrosion of copper in 1M H<sub>2</sub>SO<sub>4</sub> obtained by weight loss measurements at 303 ± 1 K

<b>Name of the inhibitor</b>	<b>Concentration (ppm)</b>	<b>Weight loss (g)</b>	<b>Inhibition efficiency (%)</b>	<b>Degree of Surface coverage (θ)</b>	<b>Corrosion rate (mpy)</b>
<b>BLANK</b>	-	0.0375	-	-	2170.29
<b>EPBD</b>	10	0.0098	73.86	0.7386	567.17
	50	0.0083	77.86	0.7786	480.35
	100	0.007	81.33	0.8133	405.12
	150	0.0048	87.20	0.8720	277.79
	200	0.0018	95.20	0.9520	104.17
<b>DPBD</b>	10	0.0146	61.06	0.6106	844.96
	50	0.013	65.33	0.6533	752.36
	100	0.0105	72.00	0.7200	607.68
	150	0.0085	77.33	0.7733	491.93
	200	0.0059	84.26	0.8426	341.46
<b>PBD</b>	10	0.0102	72.80	0.7280	590.32
	50	0.0093	75.20	0.7520	538.23
	100	0.0066	82.40	0.8240	590.32
	150	0.0049	86.93	0.8693	283.58
	200	0.0039	89.6	0.8960	225.71

**Table 6.2** Inhibition efficiencies of various concentrations of benzodiazepines for corrosion of aluminium in 1M H<sub>2</sub>SO<sub>4</sub> obtained by weight loss measurements at 303 ± 1 K

<b>Name of the inhibitor</b>	<b>Concentration (ppm)</b>	<b>Weight loss (g)</b>	<b>Inhibition efficiency (%)</b>	<b>Degree of Surface coverage (θ)</b>	<b>Corrosion rate (mpy)</b>
<b>BLANK</b>	-	0.0103	-	-	1973.94
<b>EPBD</b>	10	0.0044	57.28	0.5728	843.23
	50	0.0037	64.07	0.6407	709.08
	100	0.0032	68.93	0.6893	613.26
	150	0.0029	71.84	0.7184	555.77
	200	0.0024	76.69	0.7669	459.94
<b>DPBD</b>	10	0.0078	24.27	0.427	1494.83
	50	0.006	41.74	0.4174	1149.87
	100	0.0049	52.42	0.5242	939.06
	150	0.0042	59.22	0.5922	804.90
	200	0.0038	63.10	0.6310	728.25
<b>PBD</b>	10	0.006	41.74	0.4174	1149.87
	50	0.0049	52.42	0.5242	939.06
	100	0.0041	60.19	0.6019	1149.87
	150	0.0036	65.04	0.6504	689.92
	200	0.003	70.87	0.7087	574.93

**Table 6.3** Inhibition efficiencies of various concentrations of the benzodiazepines for corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> obtained by weight loss measurements at 303 ± 1 K

<b>Name of the inhibitor</b>	<b>Concentration (ppm)</b>	<b>Weight loss (g)</b>	<b>Inhibition efficiency (%)</b>	<b>Degree of Surface coverage (θ)</b>	<b>Corrosion rate (mpy)</b>
<b>BLANK</b>		0.2656	-	-	17466.71
<b>EPBD</b>	10	0.0769	71.04	0.7104	5057.19
	50	0.0628	76.35	0.7635	4129.93
	100	0.0435	83.62	0.8362	2860.7
	150	0.0346	86.97	0.8697	2275.40
	200	0.0135	94.91	0.9491	887.80
<b>DPBD</b>	10	0.1185	55.38	0.5538	7792.942
	50	0.0986	62.87	0.6287	6484.254
	100	0.0865	67.43	0.6743	5688.519
	150	0.0765	71.19	0.7119	5030.887
	200	0.06	77.40	0.7740	3945.793
<b>PBD</b>	10	0.0875	67.05	0.6705	5754.28
	50	0.0735	72.32	0.7232	4833.59
	100	0.0615	76.84	0.7684	4044.43
	150	0.0473	82.19	0.8219	3110.6
	200	0.0366	86.21	0.8621	2406.93

**Table 6.4** Corrosion parameters for copper in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 200 ppm of benzodiazepines from weight loss measurements at different temperatures.

Name of the inhibitor	Concentration (ppm)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage ( $\theta$ )	Corrosion rate (mpy)
<b>BLANK</b>	303	0.0125	-	-	2170.29
	313	0.0325	-	-	5642.77
	323	0.0495	-	-	8594.37
	333	0.0677	-	-	11754.33
<b>EPBD</b>	303	0.0006	95.20	0.9520	104.17
	313	0.004	87.69	0.8769	694.49
	323	0.011	77.77	0.7777	1909.86
	333	0.0266	60.70	0.6070	4618.39
<b>DPBD</b>	303	0.0019	84.80	0.8480	329.88
	313	0.007	78.46	0.7846	1215.36
	323	0.016	67.67	0.6767	2777.98
	333	0.035	48.30	0.4830	6076.83
<b>PBD</b>	303	0.0013	89.6	0.8960	225.71
	313	0.006	81.53	0.8153	1041.74
	323	0.018	63.63	0.6363	3125.22
	333	0.033	51.25	0.5125	5729.58

**Table 6.5** Corrosion parameters for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 200 ppm of benzodiazepines from weight loss measurements at different temperatures.

Name of the inhibitor	Concentration (ppm)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
<b>BLANK</b>	303	0.0034	-	-	1954.78
	313	0.0089	-	-	5116.92
	323	0.0121	-	-	6956.71
	333	0.0135	-	-	7761.06
<b>EPBD</b>	303	0.0008	76.47	0.7647	459.94
	313	0.0034	61.79	0.6179	1954.78
	323	0.0054	55.37	0.5537	3104.65
	333	0.0078	42.22	0.4222	4484.49
<b>DPBD</b>	303	0.0012	64.70	0.6470	689.92
	313	0.004	55.05	0.5505	2299.74
	323	0.0065	46.28	0.4628	3737.08
	333	0.0086	36.29	0.3629	4944.44
<b>PBD</b>	303	0.001	70.58	0.7058	574.93
	313	0.0036	59.55	0.5955	2069.76
	323	0.006	50.41	0.5041	3449.61
	333	0.008	40.74	0.4074	4599.48



**Table 6.6** Corrosion parameters for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 200 ppm of benzodiazepines from weight loss measurements at different temperatures.

<b>Name of the inhibitor</b>	<b>Temperature (K)</b>	<b>Weight loss (g)</b>	<b>Inhibition efficiency (%)</b>	<b>Degree of Surface coverage (θ)</b>	<b>Corrosion rate (mpy)</b>
<b>EPBD</b>	303	0.0045	94.91	0.9491	887.7969
	313	0.0213	81.51	0.7609	4202.23
	323	0.0345	76.09	0.7609	6806.44
	333	0.0788	68.30	0.6830	15546.31
<b>DPBD</b>	303	0.02	77.40	0.7740	3945.76
	313	0.0413	64.14	0.6414	8148.00
	323	0.0645	55.30	0.5530	12725.09
	333	0.1286	48.27	0.4827	25371.26
<b>PBD</b>	303	0.0122	86.21	0.8621	2406.91
	313	0.032	72.22	0.7222	6313.22
	323	0.0504	65.07	0.6507	9943.32
	333	0.1040	58.16	0.5816	20517.97

**Table 6.7** Thermodynamic parameters for the corrosion of copper in 1M H<sub>2</sub>SO<sub>4</sub> at 200 ppm concentration of the benzodiazepines

Name of the inhibitor	E <sub>a</sub> (kJ/mol)	ΔG* (kJ/mol)	ΔH* (kJ/mol)	ΔS* (kJ mol <sup>-1</sup> K <sup>-1</sup> )
<b>BLANK</b>	46.36	-23.83	43.84	0.22
<b>EPBD</b>	113.51	-27.16	110.98	0.45
<b>DPBD</b>	80.50	-25.86	77.98	0.34
<b>PBD</b>	101.48	-26.31	98.96	0.41

**Table 6.8** Thermodynamic parameters for the corrosion of Aluminium in 1M H<sub>2</sub>SO<sub>4</sub> at 200 ppm concentration of the benzodiazepines

Name of the inhibitor	E <sub>a</sub> (kJ/mol)	ΔG* (kJ/mol)	ΔH* (kJ/mol)	ΔS* (kJ mol <sup>-1</sup> K <sup>-1</sup> )
<b>BLANK</b>	37.71	-23.94	35.19	0.19
<b>EPBD</b>	63.08	-25.53	60.56	0.28
<b>DPBD</b>	81.19	-25.03	78.67	0.34
<b>PBD</b>	79.80	-25.31	77.28	0.33

**Table 6.9** Thermodynamic parameters for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> at 200 ppm concentration of the benzodiazepines

Name of the inhibitor	E <sub>a</sub> (kJ/mol)	ΔG* (kJ/mol)	ΔH* (kJ/mol)	ΔS* (kJ mol <sup>-1</sup> K <sup>-1</sup> )
BLANK	27.7	-21.56	25.18	0.15
EPBD	79.82	-24.81	77.30	0.33
DPBD	79.73	-23.18	77.21	0.33
PBD	78.09	-23.72	75.57	0.32

**Table 6.10** Langmuir adsorption isotherm parameters for benzodiazepines on copper at 303 ± 1 K

Compound	K <sub>ads</sub> (M <sup>-1</sup> ) X 10 <sup>4</sup>	R <sup>2</sup>	-ΔG <sup>o</sup> <sub>ads</sub> (kJ/mol)
EPBD	5.0	0.9956	37.38
DPBD	2.5	0.9906	35.63
PBD	5.0	0.9983	37.38

**Table 6.11** Langmuir adsorption isotherm parameters for benzodiazepines on aluminium at 303 ± 1 K

Compound	K <sub>ads</sub> (M <sup>-1</sup> ) X 10 <sup>4</sup>	R <sup>2</sup>	-ΔG <sup>o</sup> <sub>ads</sub> (kJ/mol)
EPBD	3.3	0.9948	36.33
DPBD	1.0	0.9909	33.32
PBD	1.42	0.9918	34.20

**Table 6.12** Langmuir adsorption isotherm parameters for benzodiazepines on mild steel at 303 ± 1 K

Compound	K <sub>ads</sub> (M <sup>-1</sup> ) X 10 <sup>4</sup>	R <sup>2</sup>	-ΔG <sup>o</sup> <sub>ads</sub> (kJ/mol)
EPBD	3.3	0.9930	36.33
DPBD	2.5	0.9922	35.63
PBD	3.3	0.9961	36.33

**Table 6.13** Impedance parameters for corrosion of copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepines at 303 ± 1 K.

Name of the inhibitor	Concentration (ppm)	R <sub>t</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μ F/cm <sup>2</sup> )	Inhibition efficiency (%)
<b>BLANK</b>	-	42.00	67.5	-
<b>EPBD</b>	10	48.00	58.4	12.50
	100	52.00	47.9	19.23
	200	53.00	29.1	20.75
<b>DPBD</b>	10	71.00	66.0	40.08
	100	88.00	65.0	52.27
	200	105.00	61.0	60.00
<b>PBD</b>	10	58.00	90.2	27.58
	100	62.00	55.2	30.00
	200	68.00	55.0	38.23

**Table 6.14** Impedance parameters for corrosion of aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepines at 303 ± 1 K.

Name of the inhibitor	Concentration (ppm)	R <sub>t</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μ F/cm <sup>2</sup> )	Inhibition efficiency (%)
<b>BLANK</b>	-	80.00	38.80	-
<b>EPBD</b>	10	140.00	18.05	42.85
	100	178.00	17.32	55.00
	200	190.00	15.77	57.87
<b>DPBD</b>	10	100.00	18.11	20.00
	100	120.00	17.45	33.33
	200	150.00	16.25	46.66
<b>PBD</b>	10	130.00	16.62	38.46
	100	140.00	16.21	42.85
	200	142.00	14.32	43.66

**Table 6.15** Impedance parameters for corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepines at 303 ± 1 K.

<b>Name of the inhibitor</b>	<b>Concentration (ppm)</b>	<b>R<sub>t</sub> (ohm cm<sup>2</sup>)</b>	<b>C<sub>dl</sub> (μ F/cm<sup>2</sup>)</b>	<b>Inhibition efficiency (%)</b>
<b>BLANK</b>	-	80.00	38.80	-
<b>EPBD</b>	10	60.00	30.8	70.00
	100	78.00	24.4	76.92
	200	120.00	19.7	85.00
<b>DPBD</b>	10	50.00	31.0	64.00
	100	78.00	29.7	76.92
	200	90.00	29.5	80.00
<b>PBD</b>	10	50.00	29.5	64.00
	100	65.00	25.2	72.30
	200	113.00	20.1	84.07

**Table 6.16** Corrosion parameters for corrosion of copper in 1M H<sub>2</sub>SO<sub>4</sub> with selected concentrations of the benzodiazepines by potentiodynamic polarization method at 303 ± 1 K.

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E <sub>corr</sub> (mV)	I <sub>corr</sub> (μAmp/cm <sup>2</sup> )	Inhibition efficiency (%)
		b <sub>a</sub>	-b <sub>c</sub>			
<b>BLANK</b>	-	58	145	40.0	410	-
<b>EPBD</b>	10	51	115	30.0	276	32.68
	100	64	131	40.0	177	56.82
	200	67	140	45.0	122	70.24
<b>DPBD</b>	10	68	160	30.0	282	31.21
	100	67	163	32.0	250	39.02
	200	66	161	34.0	220	46.34
<b>PBD</b>	10	70	145	32.0	270	34.14
	100	71	147	40.0	208	49.26
	200	67	148	43.0	165	59.75

**Table 6.17** Corrosion parameters for corrosion of aluminium in 1M H<sub>2</sub>SO<sub>4</sub> with selected concentrations of the benzodiazepines by potentiodynamic polarization method at 303 ± 1 K.

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E <sub>corr</sub> (mV)	I <sub>corr</sub> (μAmp/cm <sup>2</sup> )	Inhibition efficiency (%)
		b <sub>a</sub>	-b <sub>c</sub>			
<b>BLANK</b>	-	250.03	186.50	-680	552.00	-
<b>EPBD</b>	10	163.55	168.3	-670	280.00	49.22
	100	158.32	156.7	-665	250.00	54.71
	200	142.6	148.32	-666	230.00	58.33
<b>DPBD</b>	10	144.20	160.20	-670	380.00	31.15
	100	139.45	158.28	-667	320.00	42.02
	200	125.14	143.75	-668	293.00	46.92
<b>PBD</b>	10	171.22	157.63	-668	295.00	46.55
	100	151.48	143.37	-666	260.00	52.89
	200	138.34	127.35	-658	269.00	51.26

**Table 6.18** Corrosion parameters for corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> with selected concentrations of the benzodiazepines by potentiodynamic polarization method at 303 ± 1 K.

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E <sub>corr</sub> (mV)	I <sub>corr</sub> (μ Amp/cm <sup>2</sup> )	Inhibition efficiency (%)
		b <sub>a</sub>	-b <sub>c</sub>			
<b>BLANK</b>	-	68	167	-480.0	414.0	
<b>EPBD</b>	10	62	159	-485.0	120.00	71.01
	100	56	157	-475.1	93.00	77.52
	200	58	163	-450.4	53.00	87.19
<b>DPBD</b>	10	60	173	-480.0	240.0	42.02
	100	58	164	-475.0	156.0	62.31
	200	52	167	-470.0	120.0	71.01
<b>PBD</b>	10	60	155	-485.0	225.0	45.65
	100	50	143	-482.0	150.0	63.76
	200	46	174	-470.0	80.00	80.67



**Table 6.19** EDX data for copper after 3 hours immersion in 1M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of 200 ppm DPBD

Name of the sample	Element	Weight (%)	Atomic weight (%)
<b>BLANK</b>	C	3.84	10.26
	O	27.49	55.13
	Cu	64.07	32.35
	Zn	4.60	2.26
<b>DPBD</b>	C	6.41	14.90
	O	33.26	58.04
	N	0.39	0.79
	Cu	55.00	24.17
	Zn	4.94	2.11

**Table 6.20** EDX data for aluminium after 3 hours immersion in 1M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of 200 ppm DPBD

Name of the sample	Element	Weight (%)	Atomic weight (%)
<b>BLANK</b>	C	7.06	10.96
	O	53.33	62.19
	S	0.18	0.11
	Al	38.44	26.57
<b>DPBD</b>	C	16.99	23.21
	O	63.33	64.94
	N	0.35	0.41
	S	0.55	0.28
	Al	17.95	10.92

**Table 6.21** EDX data for mild steel after 3 hours immersion in 1M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of 200 ppm DPBD

Name of the sample	Element	Weight (%)	Atomic weight (%)
<b>BLANK</b>	C	2.19	5.64
	O	28.38	54.92
	S	1.80	1.74
	Fe	66.78	37.02
<b>DPBD</b>	C	17.12	25.53
	O	3.33	64.61
	N	1.79	2.29
	S	0.17	0.10
	Fe	23.14	7.39

**Table 6.22** AFM data for copper surface after 3 hours of immersion in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 200 ppm DPBD

Specimen	Peak – valley height (nm)	Average roughness (nm) S <sub>a</sub>	Root mean square (nm) S <sub>q</sub>
<b>Polished copper</b>	481.43	30.74	44.08
<b>BLANK</b>	1105.8	83.98	115.06
<b>DPBD</b>	717.87	42.08	82.85

**Table 6.23** AFM data for aluminium surface after 3 hours of immersion in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 200 ppm DPBD

Specimen	Peak– valley height (nm)	Average roughness (nm) S <sub>a</sub>	Root mean square (nm) S <sub>q</sub>
<b>Polished aluminium</b>	857.212	55.42	89.6
<b>BLANK</b>	1251.97	68.05	95.72
<b>DPBD</b>	1102.68	104.84	134.78

**Table 6.24** AFM data for mild steel surface after 3 hours of immersion in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 200 ppm DPBD

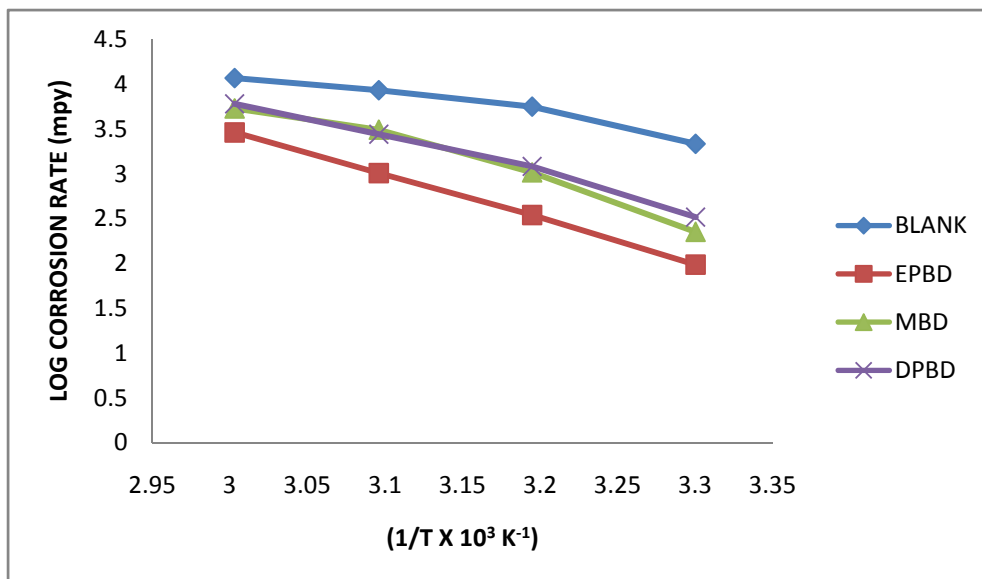
Specimen	Peak – valley height (nm)	Average roughness (nm) S <sub>a</sub>	Root mean square (nm) S <sub>q</sub>
Polished mild steel	1005.46	104.92	137.43
BLANK	1652.62	160.65	202.54
DPBD	1195.95	107.57	142.84

**Table 6.25** Excess charge on metal electrode in 1M H<sub>2</sub>SO<sub>4</sub> solution in the presence and absence of benzodiazepine

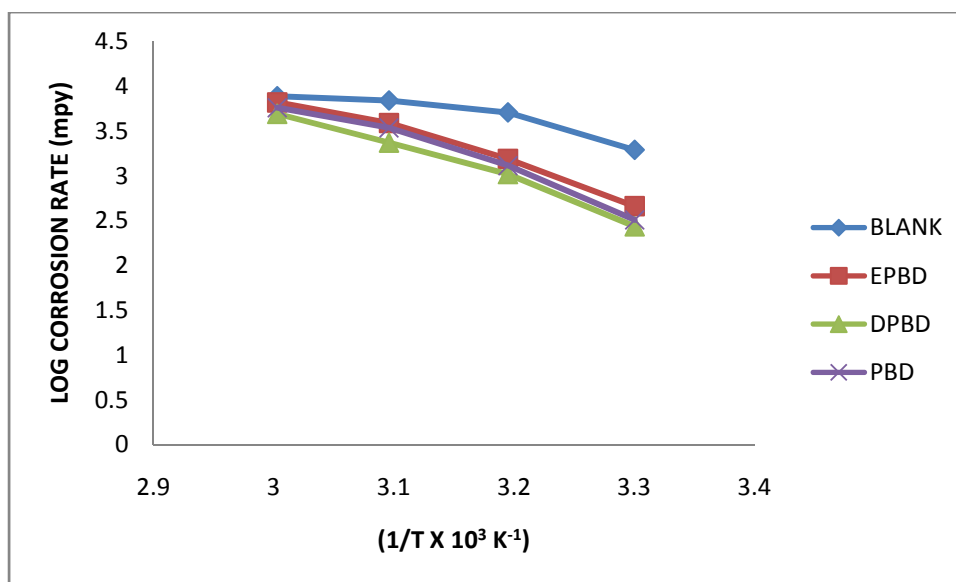
Metal	Medium	OCP (V/SCE)	PZC (V/SCE)	Excess charge $\Phi = \text{OCP} - \text{PZC}$
Copper	1M H <sub>2</sub> SO <sub>4</sub>	+ 0.04	-0.30	+ 0.34
	1M H <sub>2</sub> SO <sub>4</sub> + 200 ppm PBD	0.037	-0.3	0.337
Aluminium	1M H <sub>2</sub> SO <sub>4</sub>	-0.691	-0.7	0.009
	1M H <sub>2</sub> SO <sub>4</sub> + 200 ppm DPBD	-0.676	-0.72	0.044
Mild steel	1M H <sub>2</sub> SO <sub>4</sub>	-0.480	-0.5	0.02
	1M H <sub>2</sub> SO <sub>4</sub> + 200 ppm DPBD	-0.470	-0.55	0.08

*Figures*

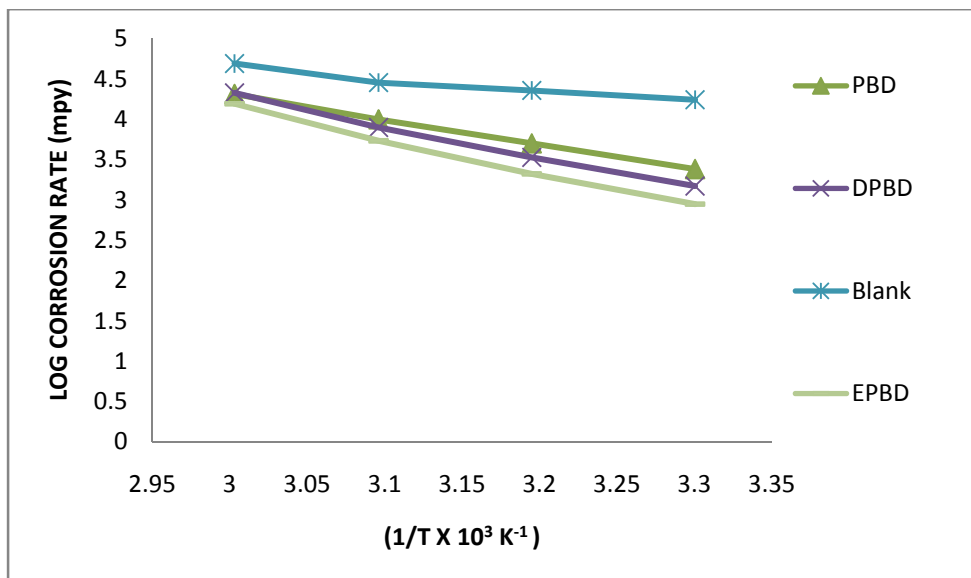
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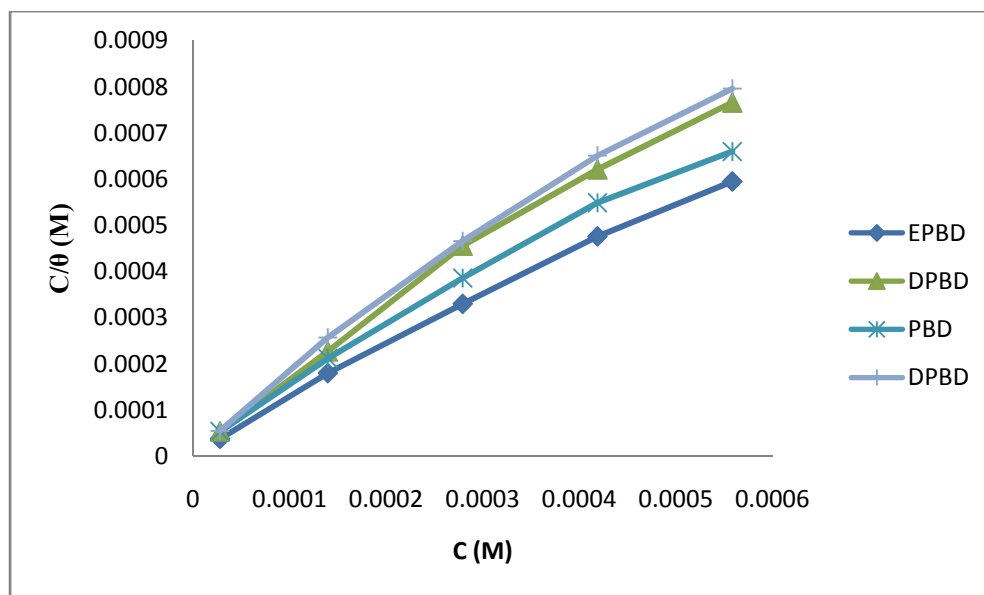
**Figure 6.1** Arrhenius plots for corrosion of copper in 1M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of benzodiazepines



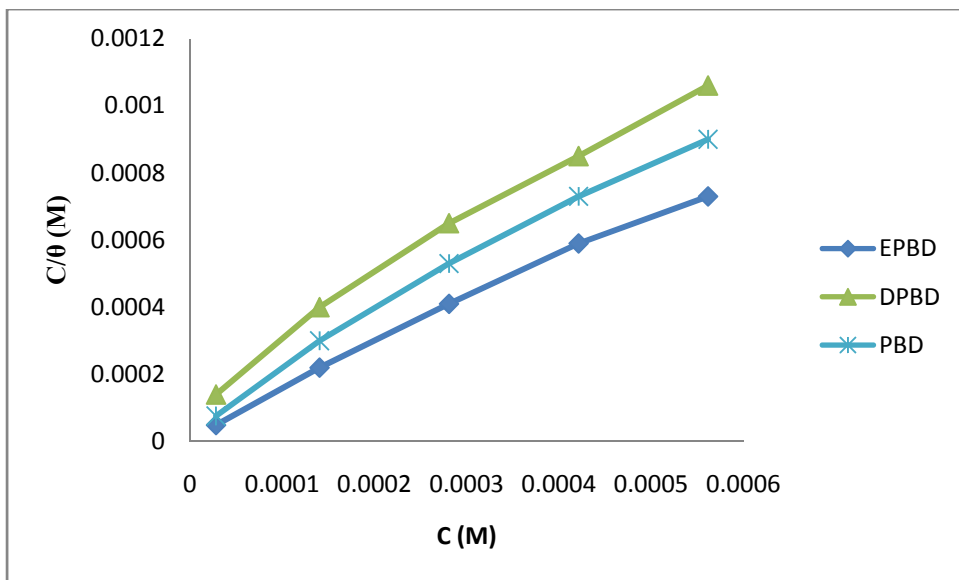
**Figure 6.2** Arrhenius plots for corrosion of aluminium in 1M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of benzodiazepines



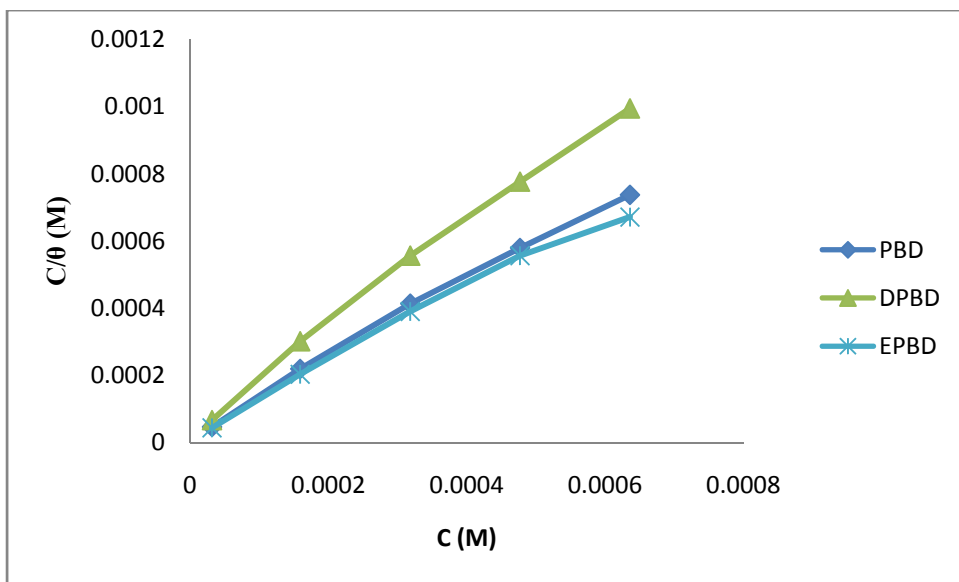
**Figure 6.3** Arrhenius plots for corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of benzodiazepines



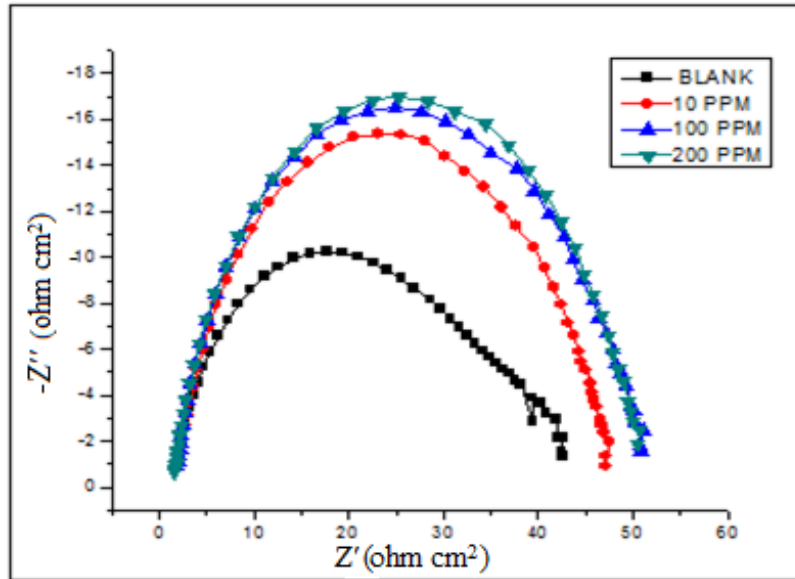
**Figure 6.4** Langmuir plots for benzodiazepines for copper corrosion in 1M H<sub>2</sub>SO<sub>4</sub>



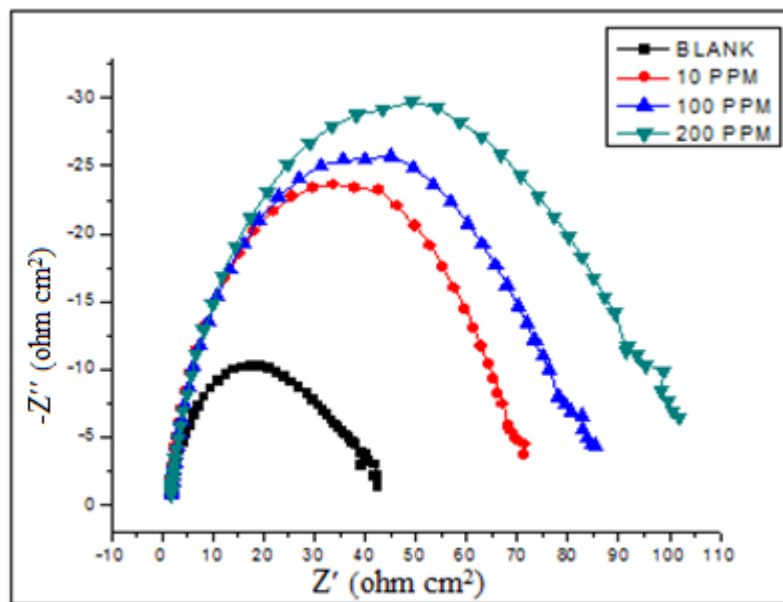
**Figure 6.5** Langmuir plots for benzodiazepines for aluminium corrosion in 1M H<sub>2</sub>SO<sub>4</sub>



**Figure 6.6** Langmuir plots for benzodiazepines for mild steel corrosion in 1M H<sub>2</sub>SO<sub>4</sub>

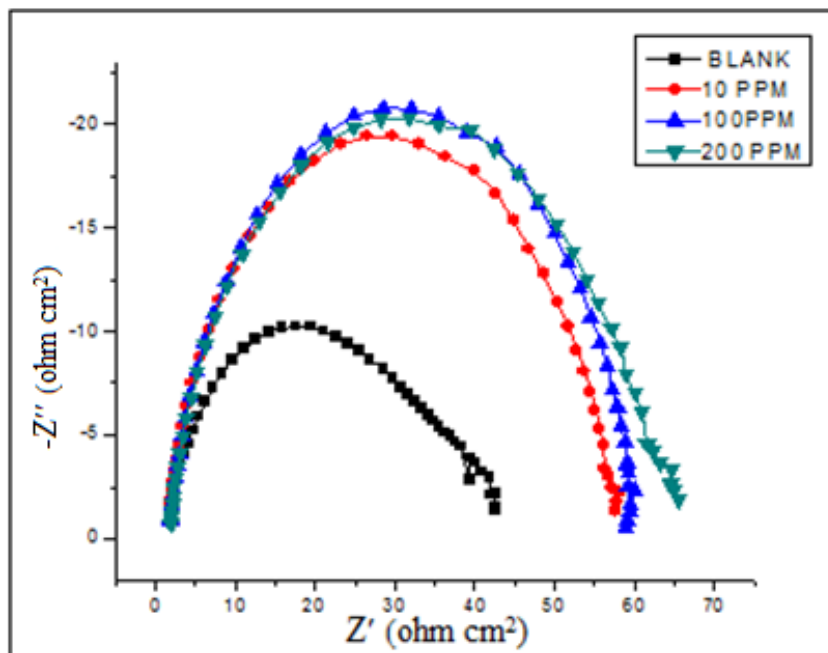


**Figure 6.7** Nyquist diagram for copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine EPBD

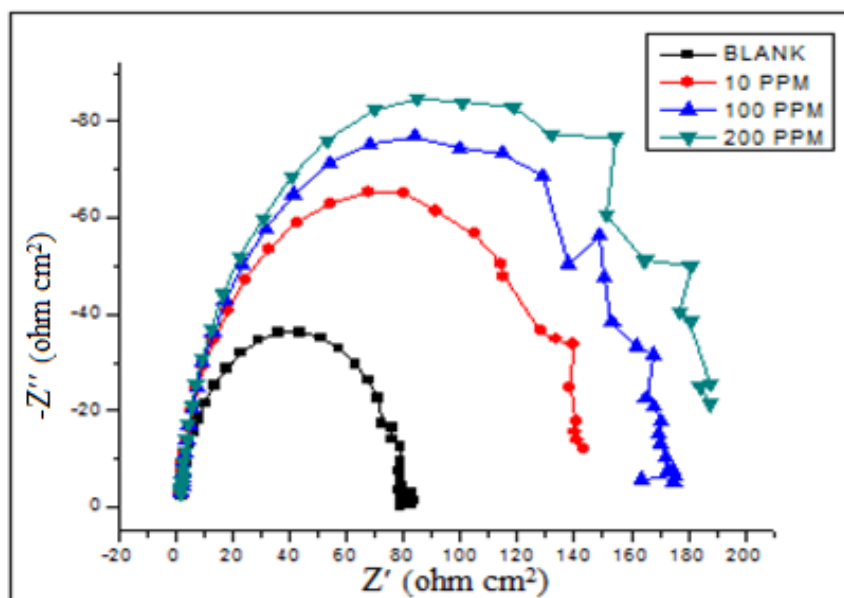


**Figure 6.8** Nyquist diagram for copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine DPBD

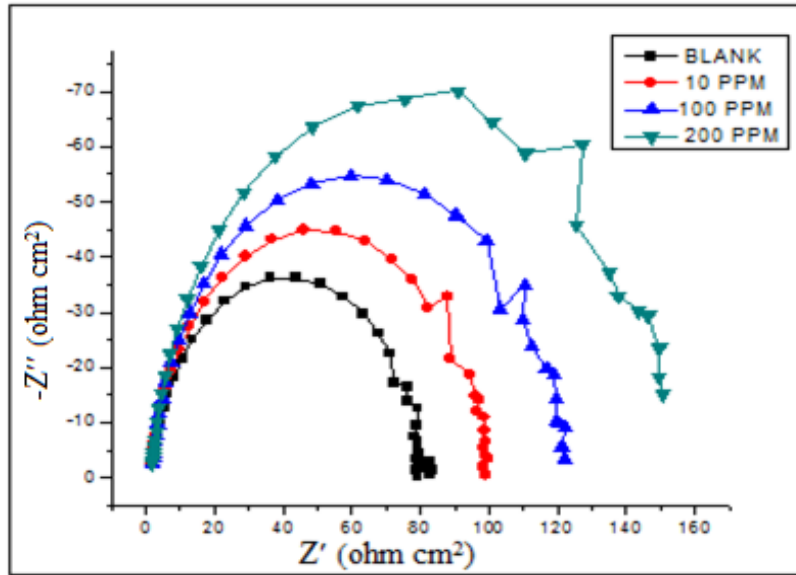




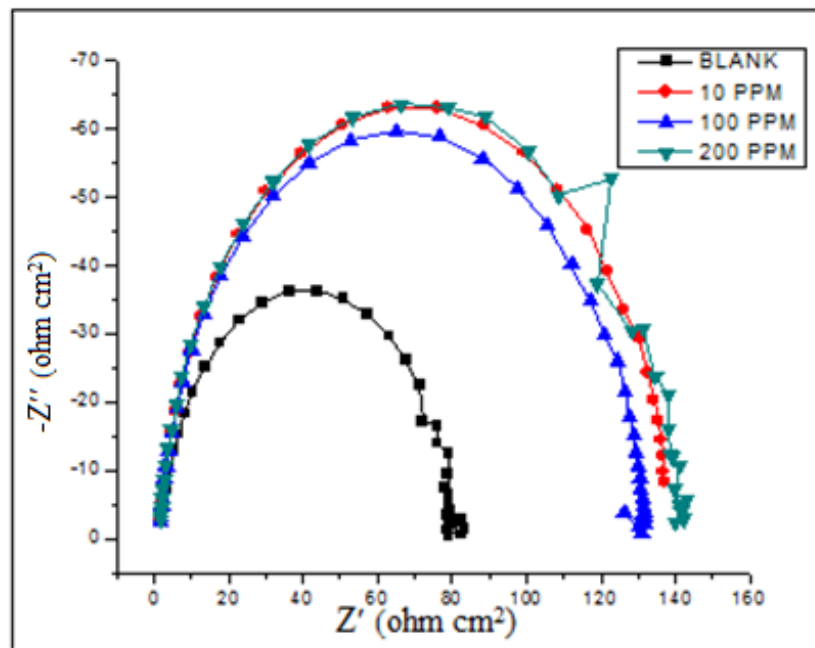
**Figure 6.9** Nyquist diagram for copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine PBD



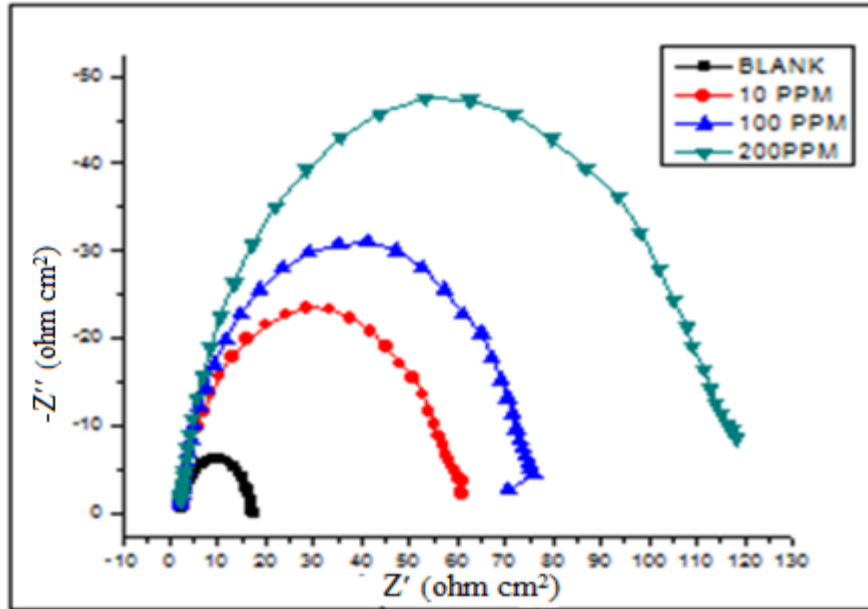
**Figure 6.10** Nyquist diagram for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine EPBD



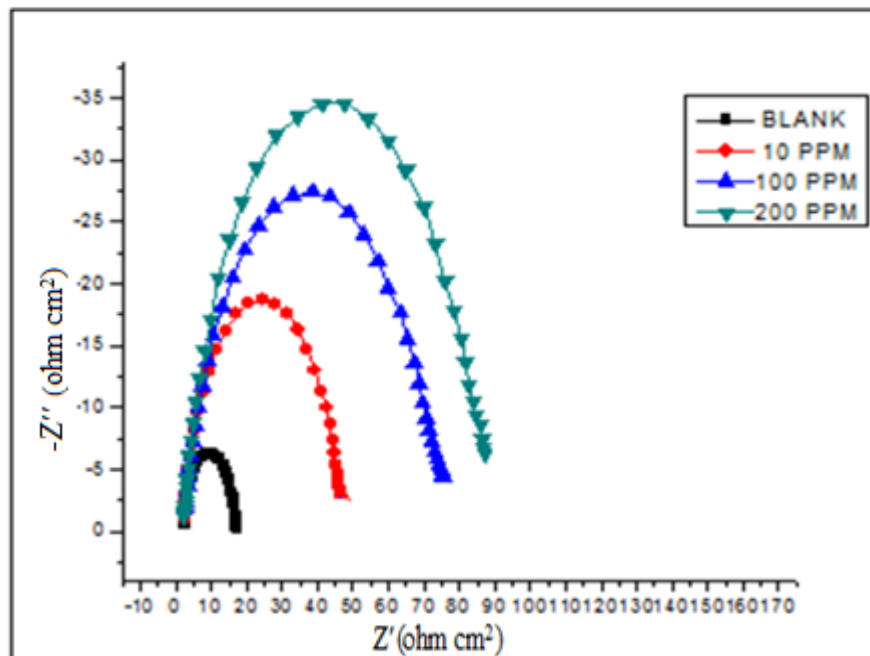
**Figure 6.11** Nyquist diagram for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine DPBD



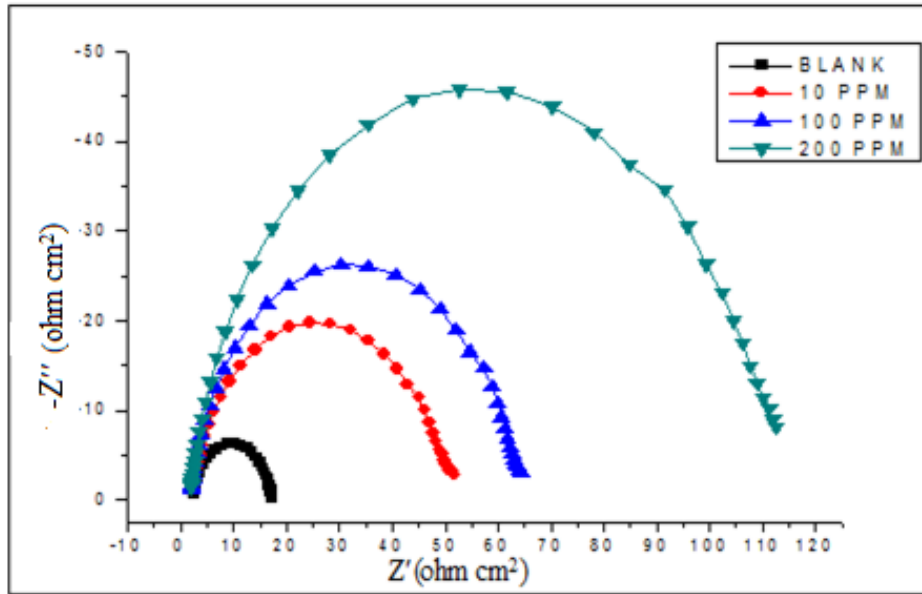
**Figure 6.12** Nyquist diagram for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine PBD



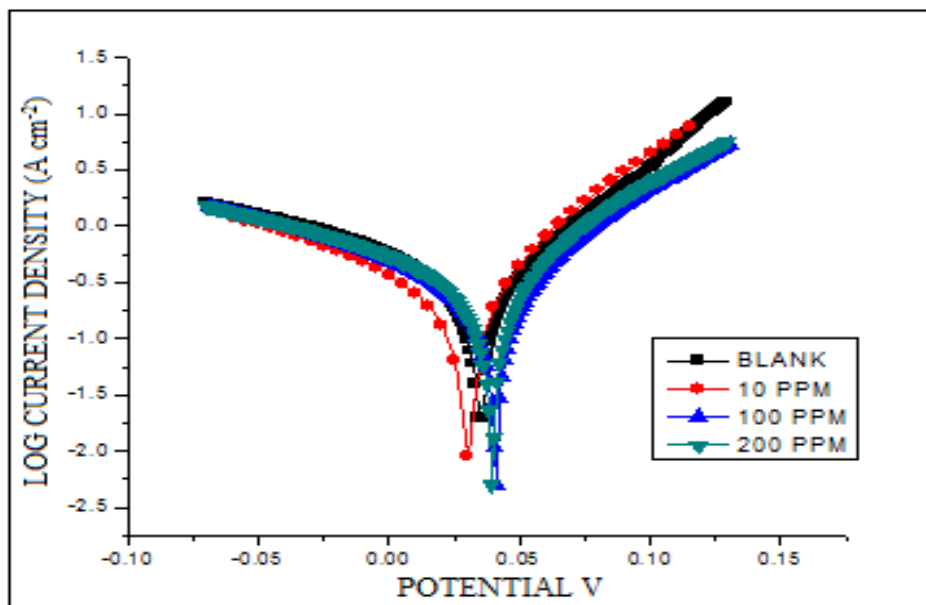
**Figure 6.13** Nyquist diagram for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine EPBD



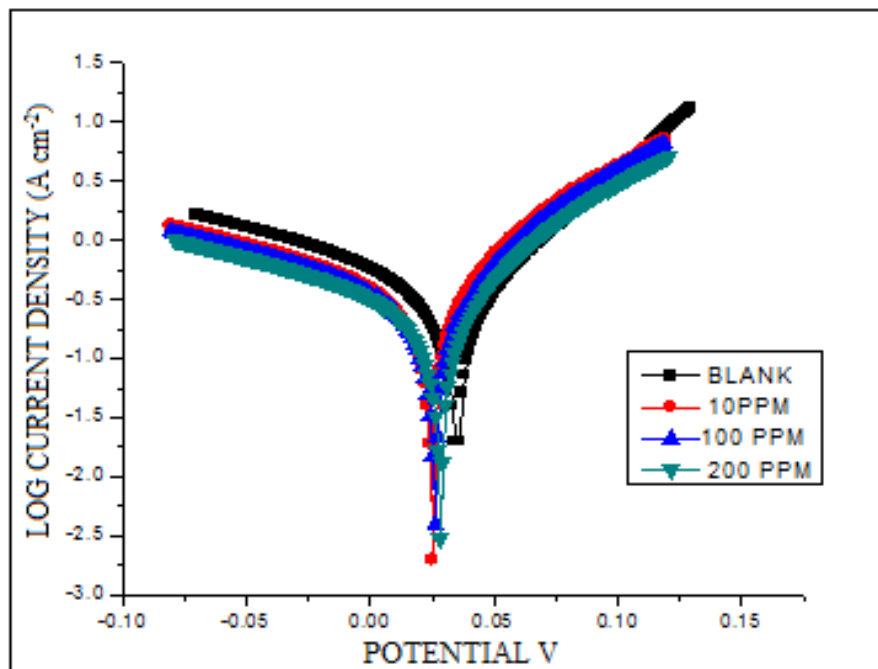
**Figure 6.14** Nyquist diagram for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine DPBD



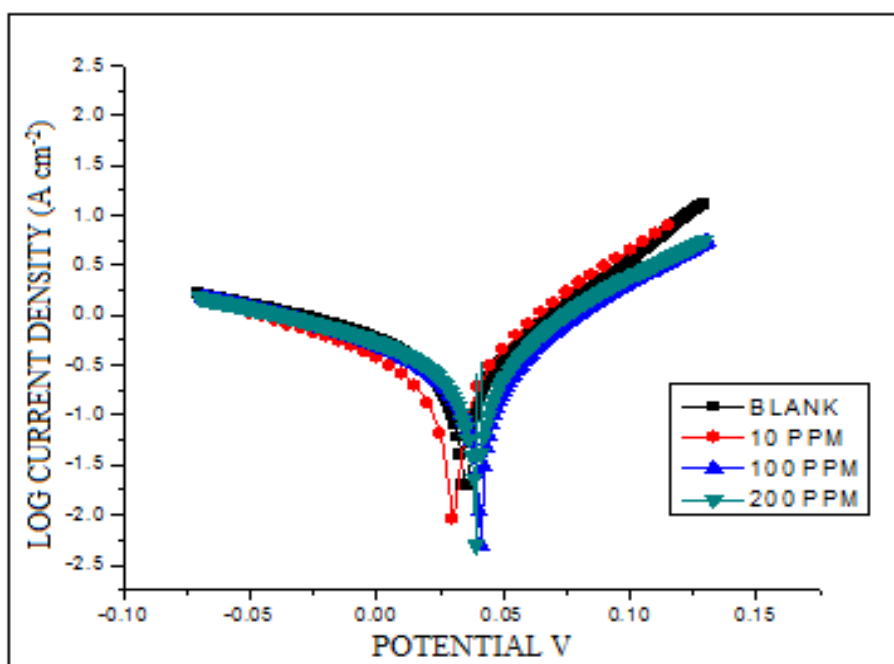
**Figure 6.15** Nyquist diagram for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine PBD



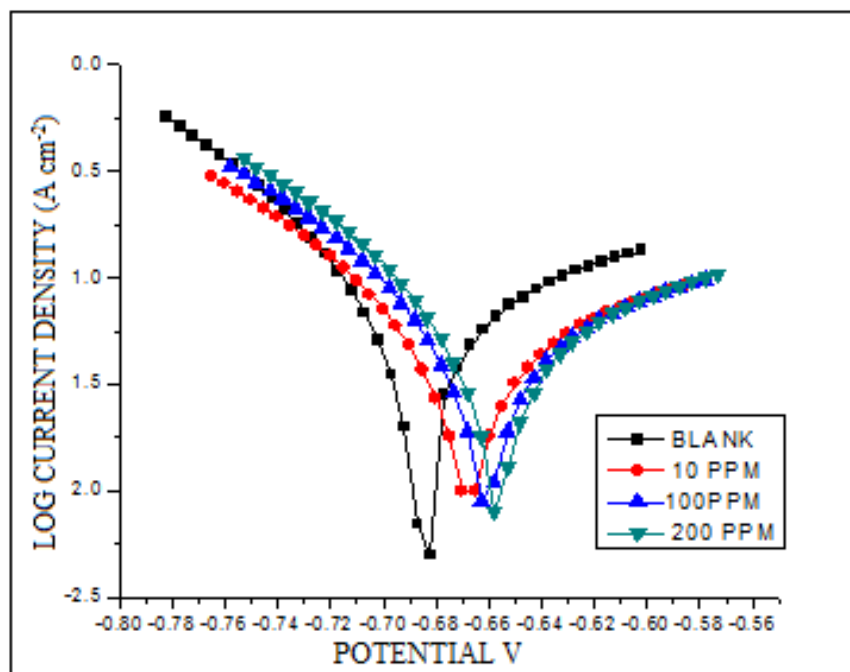
**Figure 6.16** Polarization curves for copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine EPBD



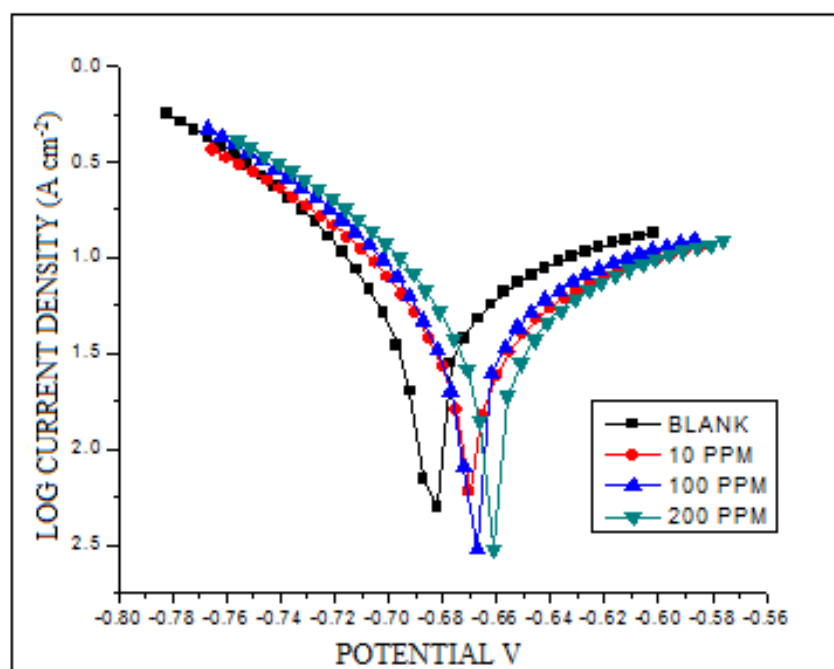
**Figure 6.17** Polarization curves for copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine DPBD



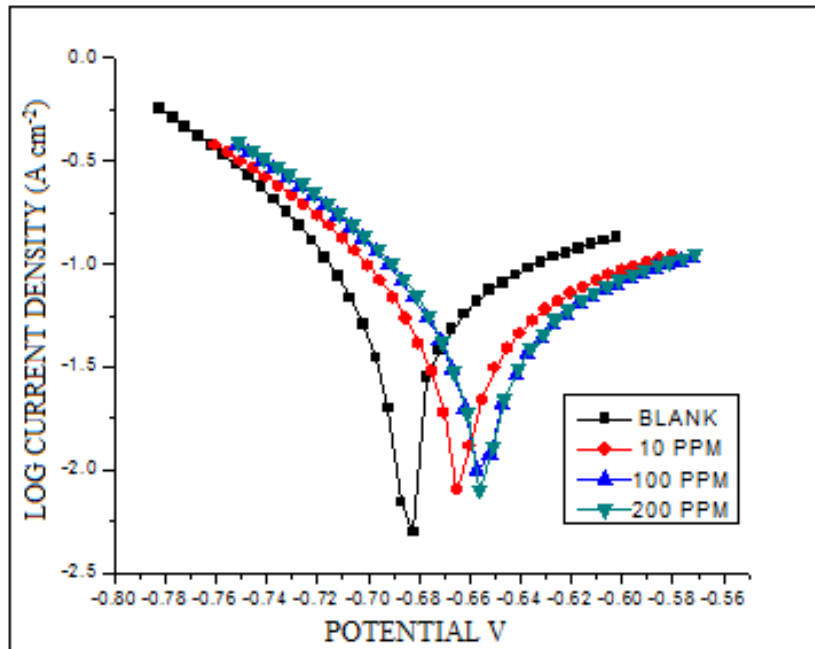
**Figure 6.18** Polarization curves for copper in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine PBD



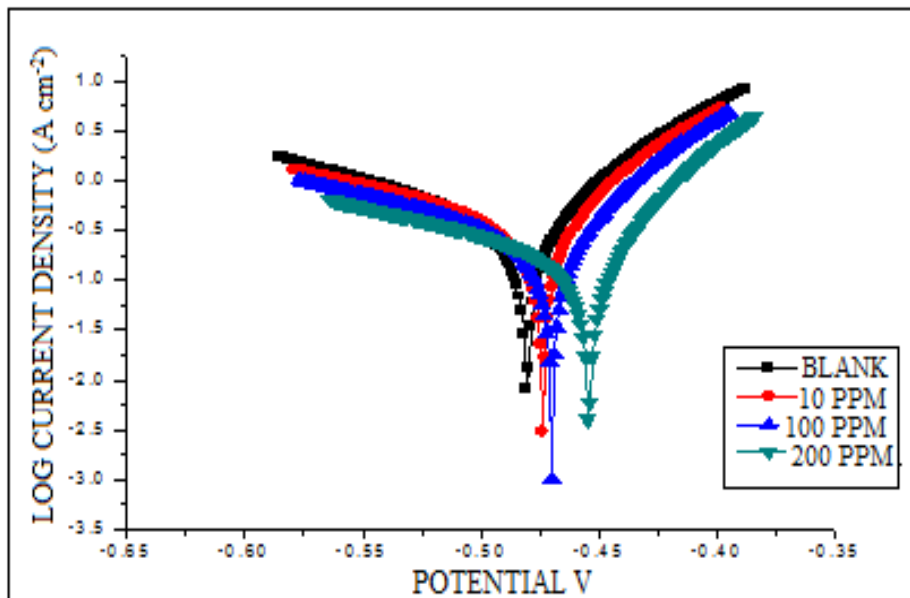
**Figure 6.19** Polarization curves for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine EPBD



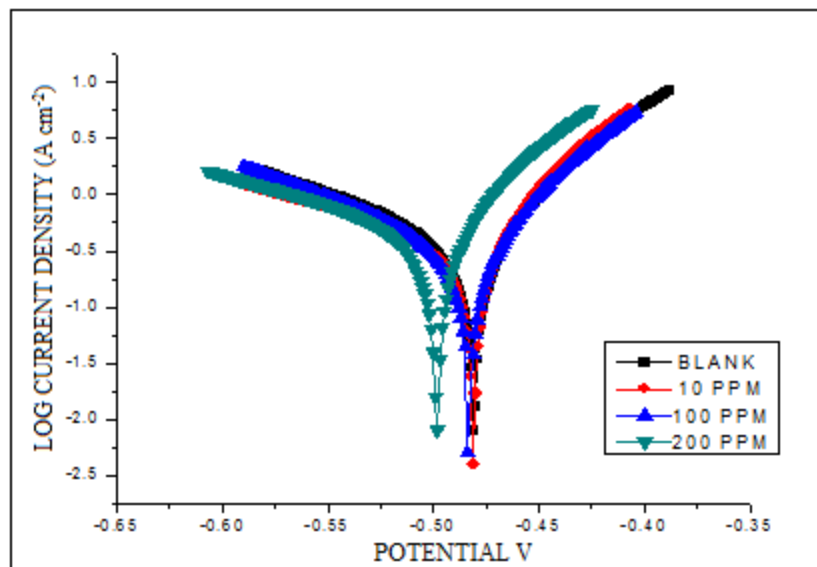
**Figure 6.20** Polarization curves for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine DPBD



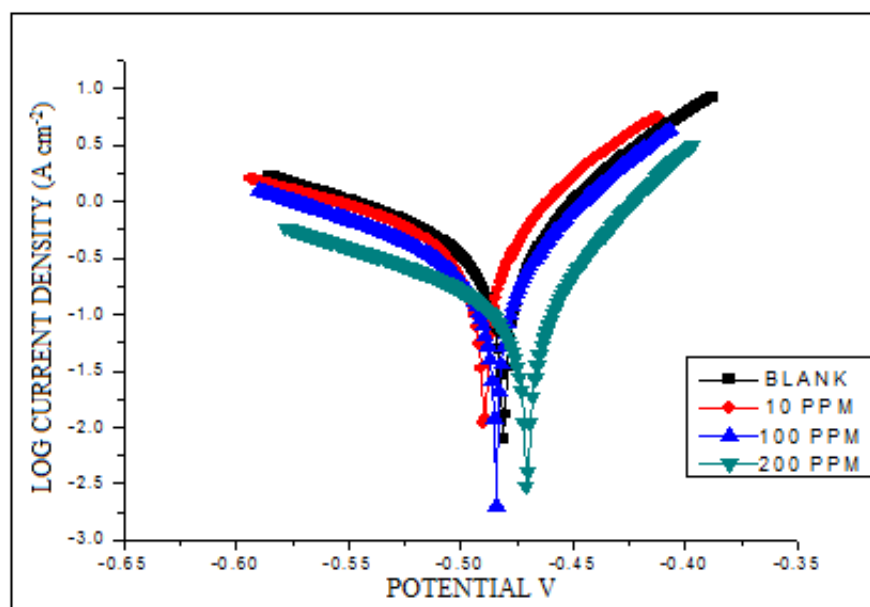
**Figure 6.21** Polarization curves for aluminium in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine PBD



**Figure 6.22** Polarization curves for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine EPBD

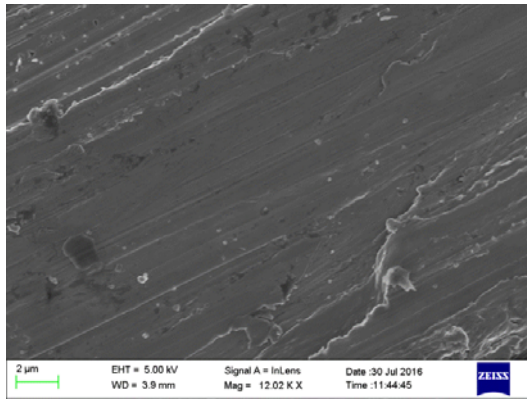


**Figure 6.23** Polarization curves for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine DPBD

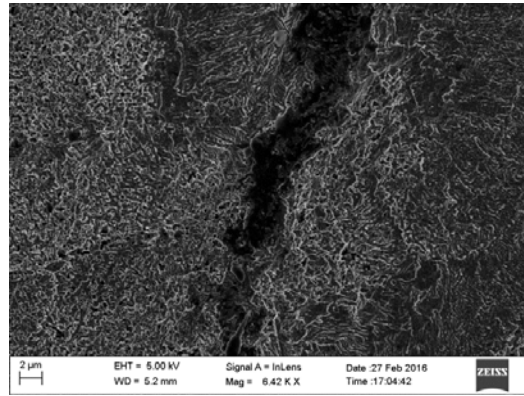


**Figure 6.24** Polarization curves for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected concentrations of benzodiazepine PBD

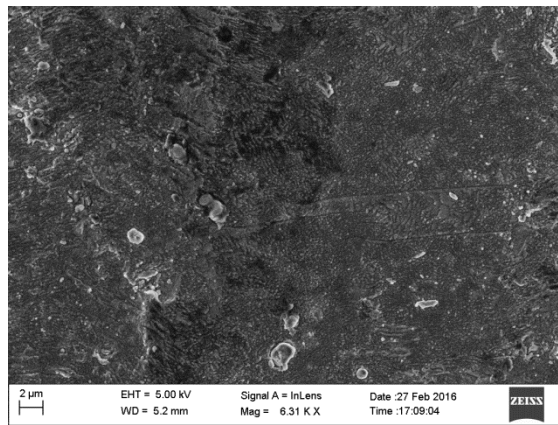




(a)

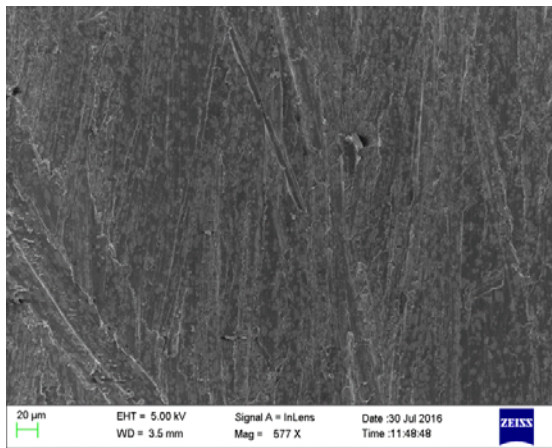


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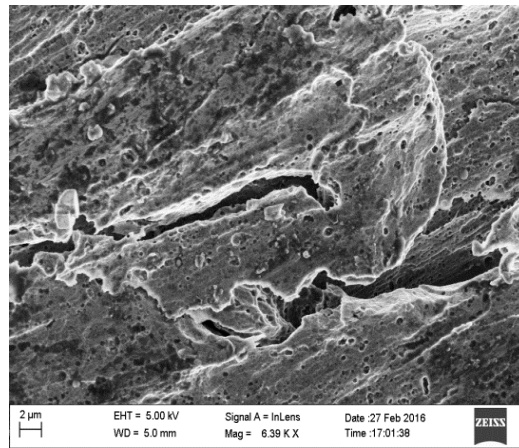


(c)

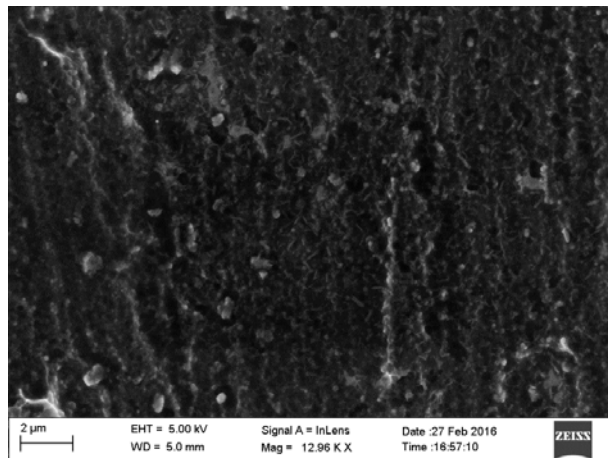
**Figure 6.25** Scanning electron micrograph of copper specimen (a) Polished (b) After immersion in 1M H<sub>2</sub>SO<sub>4</sub> (c) After immersion in 1M H<sub>2</sub>SO<sub>4</sub> containing DPBD



(a)

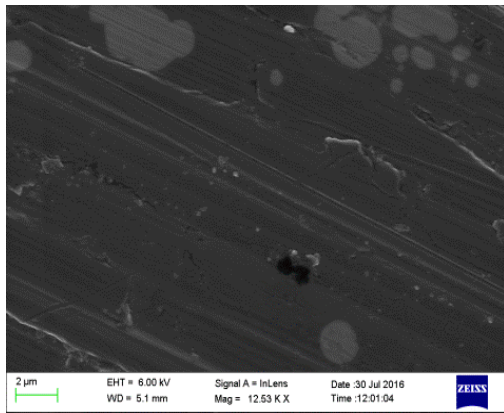


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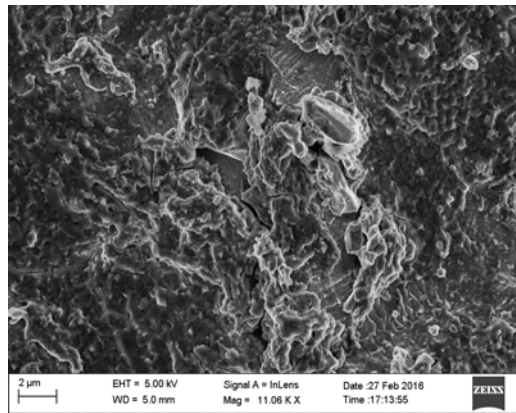


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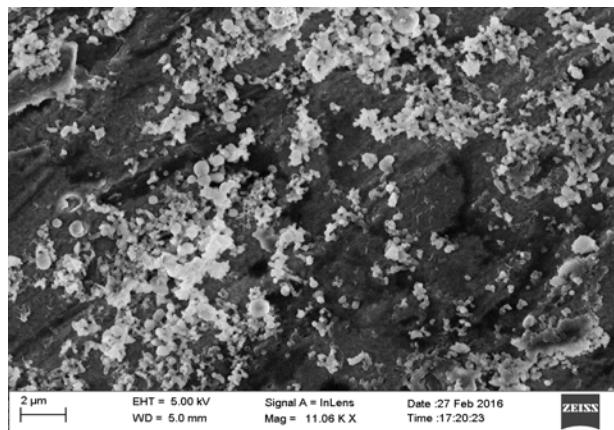
**Figure 6.26** Scanning electron micrograph of aluminium specimen (a) Polished (b) After immersion in 1M  $H_2SO_4$  (c) After immersion in 1M  $H_2SO_4$  containing DPBD



(a)

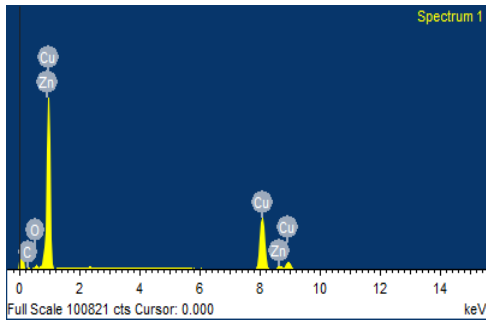


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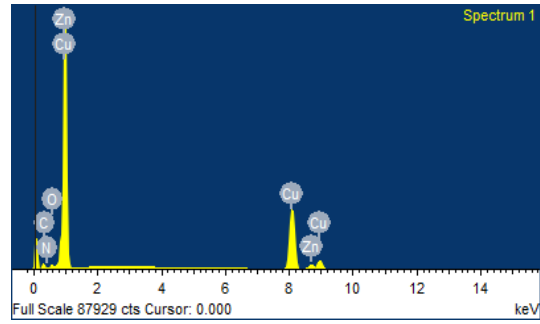


(c)

**Figure 6.27** Scanning electron micrograph of mild steel specimen (a) Polished (b) After immersion in 1M  $\text{H}_2\text{SO}_4$  (c) After immersion in 1M  $\text{H}_2\text{SO}_4$  containing DPBD

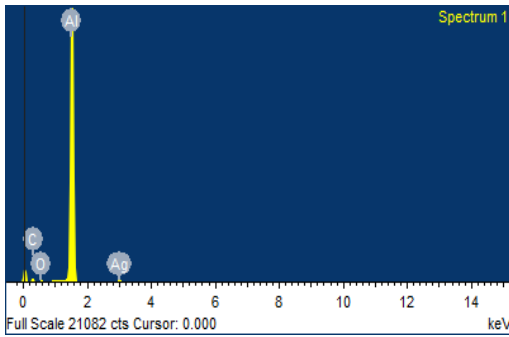


(a)

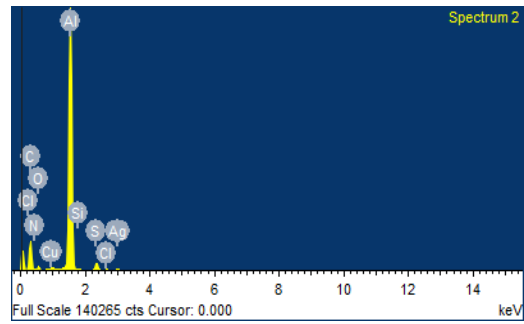


(b)

**Figure 6.28** EDX spectra of copper immersed in 1M H<sub>2</sub>SO<sub>4</sub> containing (a) 1M H<sub>2</sub>SO<sub>4</sub> (b) DPBD

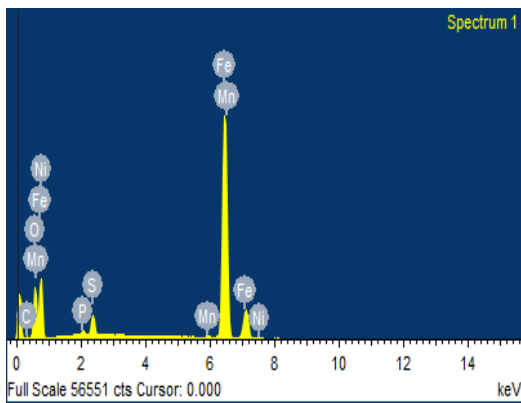


(b)

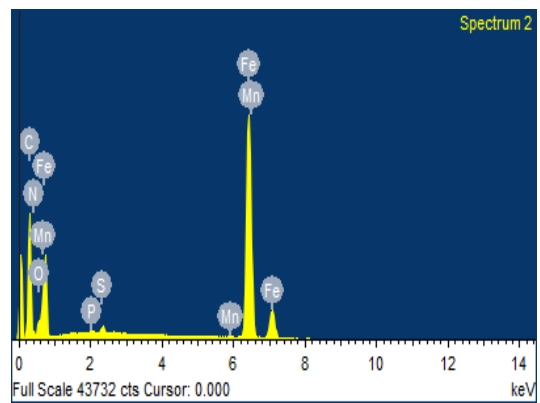


(a)

**Figure 6.29** EDX spectra of aluminium immersed in 1M H<sub>2</sub>SO<sub>4</sub> containing (a) 1M H<sub>2</sub>SO<sub>4</sub> (b) DPBD

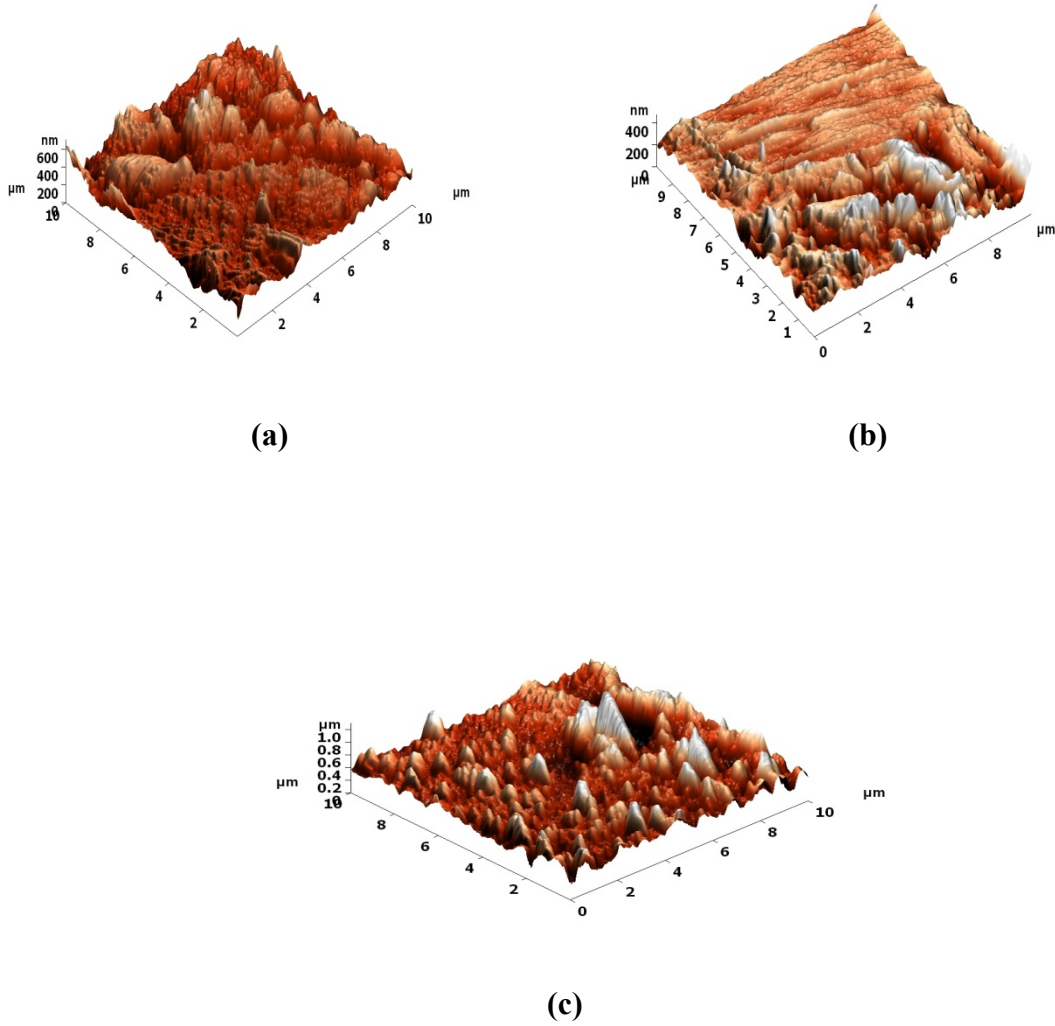


(a)

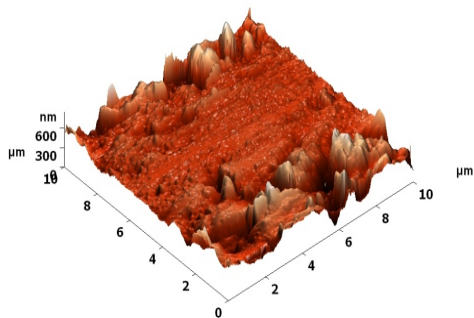


(b)

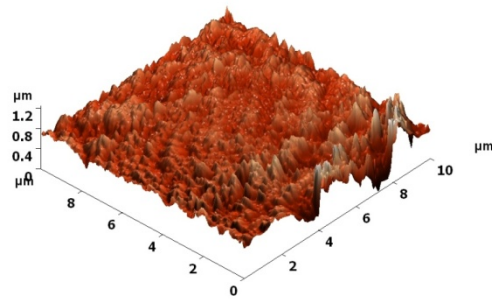
**Figure 6.30** EDX spectra of mild steel immersed in 1M H<sub>2</sub>SO<sub>4</sub> containing (a) 1M H<sub>2</sub>SO<sub>4</sub> (b) DPBD



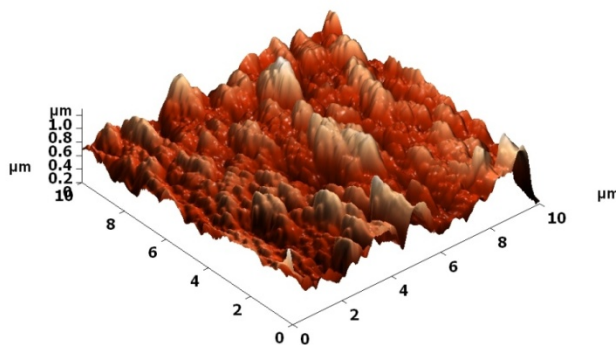
**Figure 6.31** 3D AFM topography of (a) copper (b) copper immersed in 1M  $\text{H}_2\text{SO}_4$  (c) copper immersed in 1M  $\text{H}_2\text{SO}_4$  containing DPBD



(a)

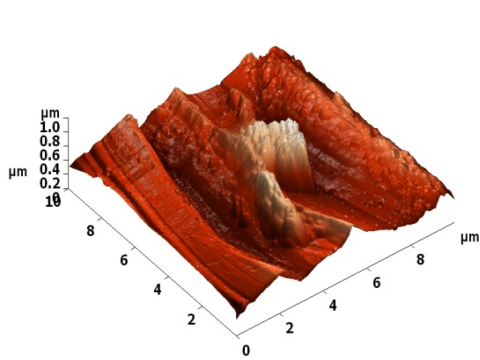


(b)

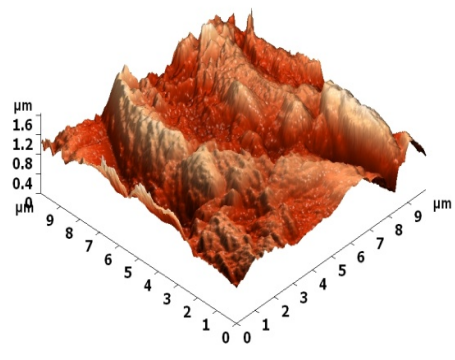


(c)

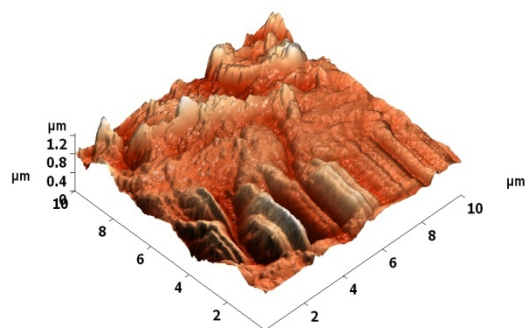
**Figure 6.32** 3D AFM topography of (a) aluminium (b) aluminium immersed in 1M H<sub>2</sub>SO<sub>4</sub> (c) aluminium immersed in 1M H<sub>2</sub>SO<sub>4</sub> containing DPBD



(a)

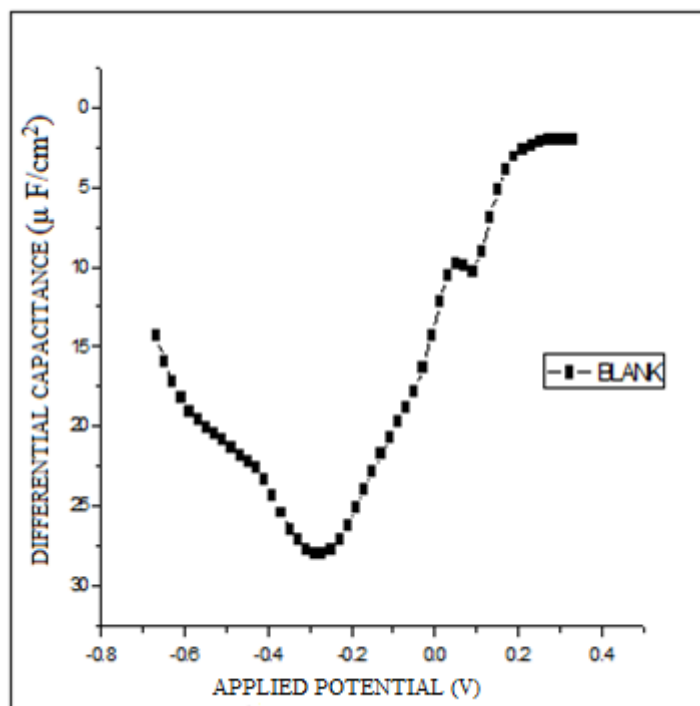


(b)

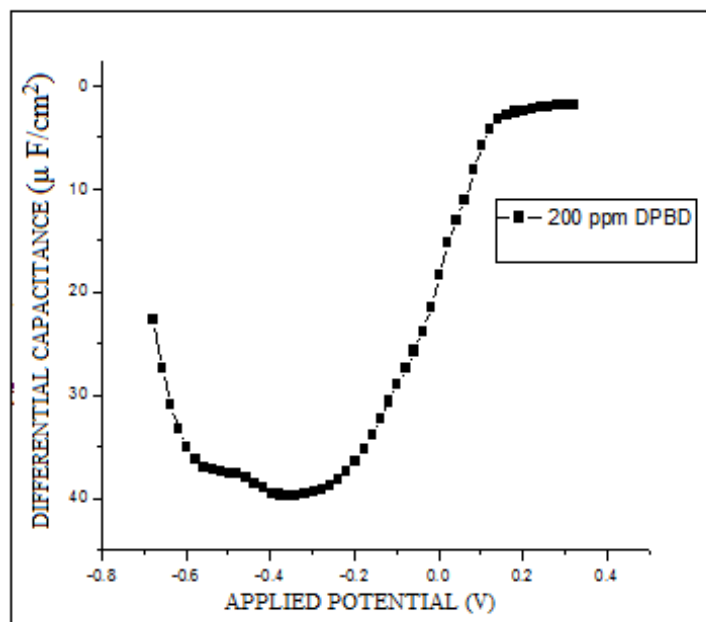


(c)

**Figure 6.33** 3D AFM topography of (a) bare mild steel (b) mild steel immersed in 1M H<sub>2</sub>SO<sub>4</sub> (c) Mild steel immersed in 1M H<sub>2</sub>SO<sub>4</sub> containing DPBD



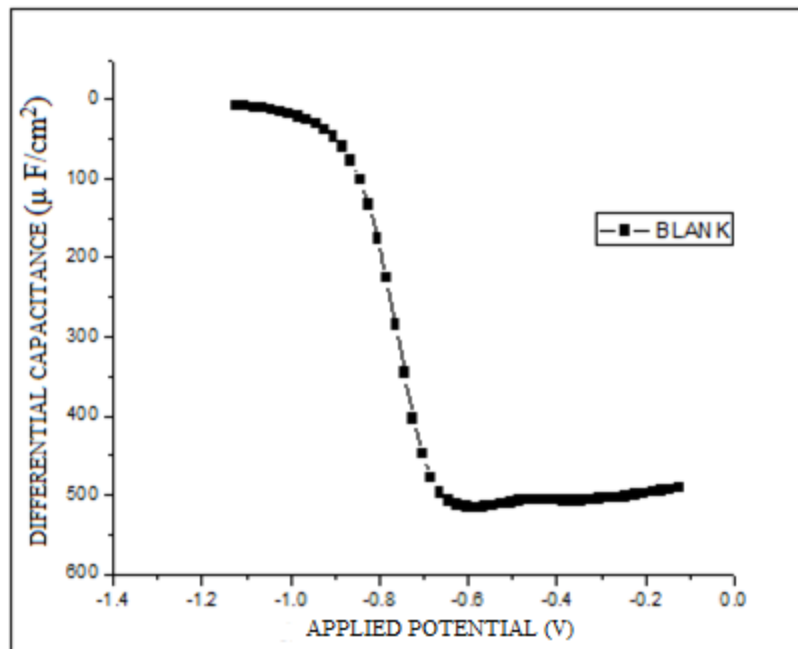
(a)



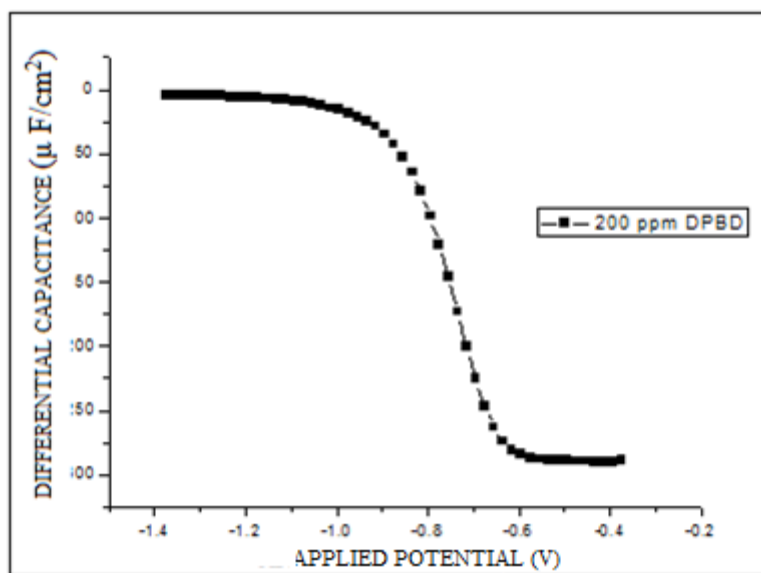
(b)

**Figure 6.34** The plot of differential capacitance vs. applied electrode potential for copper in (a) 1M H<sub>2</sub>SO<sub>4</sub> (b) 1M H<sub>2</sub>SO<sub>4</sub> containing 200 ppm of DPBD



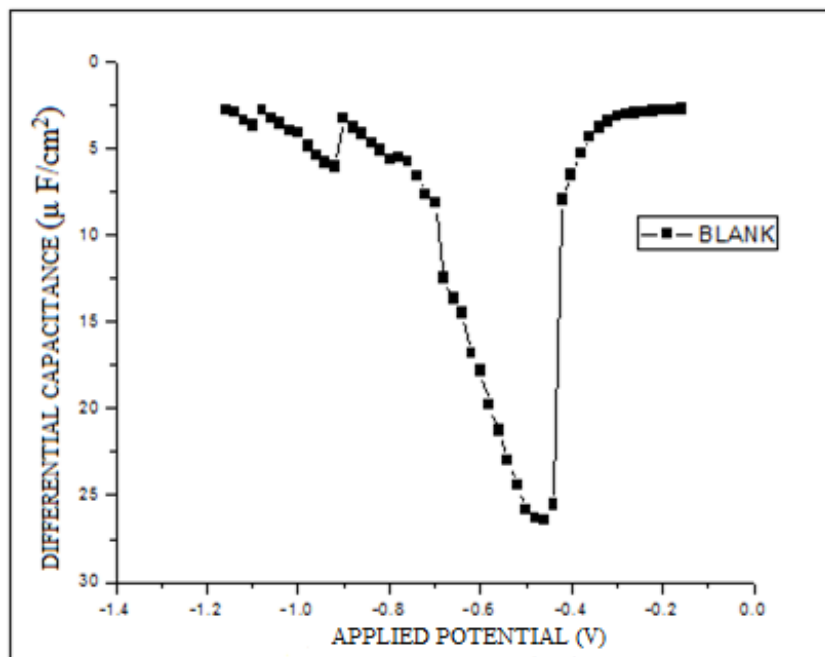


(a)

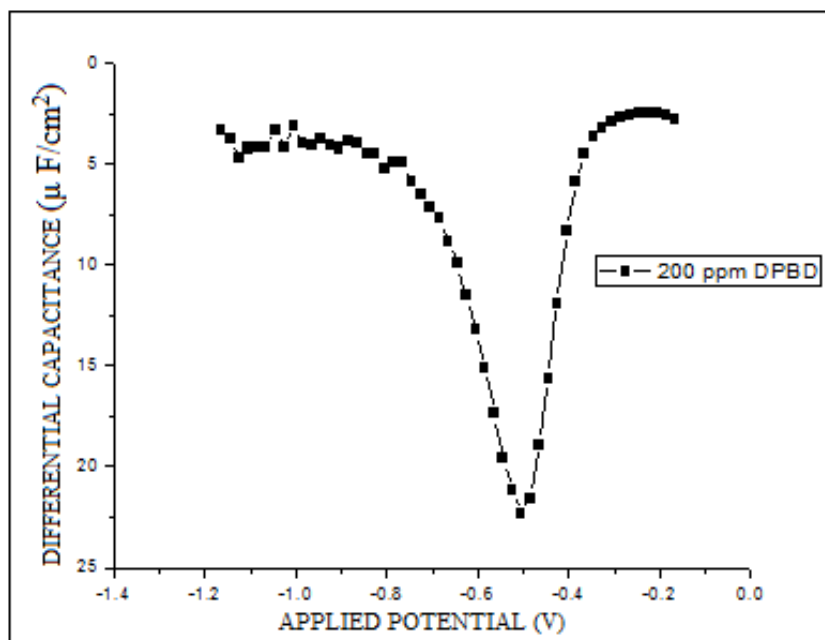


(b)

**Figure 6.35** The plot of differential capacitance vs. applied electrode potential for aluminium in (a) 1M  $\text{H}_2\text{SO}_4$  (b) 1M  $\text{H}_2\text{SO}_4$  containing 200 ppm of DPBD



(a)



(b)

**Figure 6.36** The plot of differential capacitance vs. applied electrode potential for mild steel in (a) 1M H<sub>2</sub>SO<sub>4</sub> (b) 1M H<sub>2</sub>SO<sub>4</sub> containing 200 ppm of DPBD