Chapter 5

CHAPTER-5

COMPARISON OF CORROSION INHIBITIVE PERFORMANCE OF BENZOTHIAZEPINES, BENZOXAZEPINES AND BENZODIAZEPINES

5.1 Introduction

In chapter-4, the inhibition performances of ten synthesized benzodiazepines against the corrosion of mild steel in 1M H_2SO_4 have been investigated. The results of the studies showed that the benzodiazepine moiety is the adsorption centre which interacts with the metal ions on the surface through the protonated N centre, lone pair of electrons and π-electrons of the aromatic rings. The inhibition efficiency was influenced by the substituents attached to the diazepine ring and also on the phenyl ring. In general aryl groups on the benzodiazepines enhanced the efficiency by offering additional adsorption centers and /or enhance the electron density and planar orientation of the primary adsorption centre i.e., the benzodiazepine ring.

Compounds containing both sulphur and nitrogen atoms have been reported to be better inhibitors than those containing either atom alone. For example thiourea and its derivatives have been extensively used as corrosion inhibitors in acidic media[1]. Sulphur is a better electron donor than nitrogen and has d-orbitals for back bonding with metal ions. Such compounds adsorb well on the metal surface. Moreover sulphur containing compounds perform well in sulphuric acid medium. A perusal of literature shows that benzofused five and six membered heterocyclics such as benzimidazole[2], benzothiazole[3], benzoxazole[4], benzothiazine[5], quinoxalines[6] etc., have been applied as corrosion inhibitors. No comparative study has so far been reported on the use of benzofused 7-membered systems such as benzodiazepines, benzothiazepines and benzoxazepines.

This chapter deals with the synthesis of some selected benzothiazepines and benzoxazepines and evaluation of corrosion inhibitory property for mild steel in 1M H_2SO_4. Inhibition performance has been compared with that of analogous benzodiazepine compounds.

Gravimetric and electrochemical corrosion monitoring techniques have been used. Surface morphology of mild steel specimens has been examined before and after immersion in blank 1M H_2SO_4 and 1M H_2SO_4 containing the inhibitors using scanning electron microscopy.

Table 5.1- 5.3 gives the structure and IUPAC names of the compounds.

The compounds were characterized by FTIR spectroscopy. The FTIR spectra of representative compounds are shown in Figure 5.1-5.2. The band due to stretching frequency of –C=N group around 1624 cm^{-1} is present in the FTIR spectrum of the benzothiazepine TMBTZ. The band due to –C–S stretching is observed at 1396 cm^{-1}. In addition, bands due to –C=C– is observed at 1538cm^{-1}. FTIR spectrum of benzoxazepine TMBOZ (Figure 5.2) showed bands characteristic of C=N at 1565 cm^{-1}, C=C at 1520 cm^{-1} and C-O at 1341 cm^{-1}. There is no band around 3300 cm^{-1} indicating the absence of NH group in the molecule.

5.2Weight loss studies

Tables 5.4-5.5 show the variation of inhibition efficiency and corrosion rate obtained from weight loss of mild steel in 1M H_2SO_4 with different concentrations of benzothiazepines and benzoxazepines. For comparison purpose, the corresponding data for benzodiazepines are also given (Table 5.6). Inhibition efficiency increased and corrosion rate decreased with increased concentration of inhibitors. Benzothiazepines showed good inhibition efficiency when compared to benzodiazepines and benzoxazepines at the fixed concentration range of 10 ppm-200 ppm. Benzothiazepine EPBTZ, (with OEt and –OH groups attached on phenyl ring) displayed 93% activity and MBTZ, TMBTZ, DPBTZ showed 89%, 74% and 85% inhibition efficiency respectively.

Benzoxazepines and benzodiazepines showed somewhat lower inhibition efficiency. At 200 ppm the selected benzodiazepines showed 65-94% activity and the corresponding benzoxazepines displayed 62-86% inhibition efficiency. It is evident that the heteroatoms on the 7-membered ring influence the efficiency of the compounds to inhibit the corrosion of mild steel in 1M H_2SO_4.

5.3 Effect of temperature and thermodynamic parameters

Temperature has profound influence on corrosion and inhibition. The effect of temperature on the performance of the benzofused heterocyclics has been studied in the temperature range 303-333 K with the maximum concentration tested at 303 ± 1K. The results are summarized in Table 5.7- 5.9. Corrosion rate is higher for mild steel in free acid compared to the inhibited acid at all the temperatures. The inhibition efficiency decreased with temperature. About 6-14% decrease in efficiency was noted for every 10° C rise in temperature. The decrease in % IE with increase in temperature may be attributed to physisorption of the inhibitors on mild steel which is weakened at higher temperatures leading to desorption of the molecules. Hence more sites are exposed to acid environment[7].

The activation energy E_a for corrosion of mild steel was obtained using Arrhenius equation.

$$\text{Log corrosion rate} = \frac{E_a}{2.303RT} + \log A$$

Where R is the molar gas constant, T is the absolute temperature and A is the pre exponential factor. Figure 5.3 - 5.5 represents the Arrhenius plots of the studied azepines. The slope of the lines was determined and used to calculate the activation energy [E_a = - slope * 2.303R]. The values of E_a are summarized in Table 5.10 - 5.12. It is evident that the E_a values in presence of inhibitors were higher than that in their absence. This indicates that the dissolution of mild steel was decreased due to the increased energy barrier by the adsorption of the molecules on the steel surface.

The kinetic thermodynamic parameters – ΔH^*, ΔS^* and ΔG^* are calculated for the corrosion of mild steel using the equations given in chapter- 4. The values are recorded in Table 5.10-5.12. ΔH^* values are positive suggesting the endothermic nature of mild steel dissolution in acid. The values are higher in presence of inhibitor compared to the free acid value (21.58 kJ/mol) which indicates that the corrosion is slower in the presence of inhibitor. The changes in free energy of activation are all negative and are in the range -21 kJ/mol to -26 kJ/mol. The change in entropy of activation is positive signifying that there is an increase in disorder during corrosion inhibition.

Adsorption isotherm

Adsorption isotherms and the parameters derived from them can provide additional information about the properties of the tested compounds. The degree of surface coverage values θ obtained from mass loss measurements were fitted to various adsorption isotherms. A plot of C/ θ vs. C gives straight lines for all the three classes of compounds proving that the benzoheteroazepines obey Langmuir isotherm on mild steel in 1M H_2SO_4.

The free energy of adsorption ΔG°_{ads}, equilibrium constant of adsorption (K_{ads}) and the regression coefficients (R^2) obtained from the Langmuir plots (Figure 5.6-5.8) are recorded in Tables 5.13-5.15. The ΔG°_{ads} values are greater than 30kJ/mol and are higher for benzothiazepines suggests that the adsorption of the benzothiazepine compounds involves two types of interactions i.e. there may be some charge transfer or charge sharing in addition to physisorption. Tang *et al*., have reported that similar ΔG°_{ads} values (about -33 kJ/mol) for the studied thiadiazole compounds and concluded that a mixed adsorption mechanism prevails[8]. The K_{ads} values are higher for benzothiazepines indicating their stronger adsorption on steel surface compared to benzoxazepines or benzodiazepines

5.4 Electrochemical impedance studies (EIS)

The results of EIS techniques in the form of Nyquist plots are presented in Figure (5.9-5.20). It is evident that the diameter of the semicircle representing the impedance of mild steel increases with increased inhibitor concentrations. For corrosion reactions, the impedance parameters can be obtained by curve fitting using an equivalent circuit as explained in chapter 4. The values of charge transfer resistance (R_t), double layer capacitance (C_{dl}) and percentage inhibition efficiency are listed in Table 5.16 - 5.18. The results show that R_t values increase with rising concentration of the inhibitors. The increase in R_t values has been reported to be due to more impediment of the active area at the metal surface as a result of increase in inhibitor concentration[9]. The values of double layer capacitance C_{dl} decreased by the addition of inhibitors to 1M H_2SO_4. C_{dl} was decreased to a maximum extent to 14 μ F/cm^2 for DPBTZ; 15 μ F/cm^2 for EPBOZ from the blank acid value of 38 μ F/cm^2. As explained in chapter 4.5, the decrease in double layer capacitance may be due to the replacement of water molecules by the organic molecules having lower dielectric constant[10]. The decrease may also be attributed

to the decrease in surface area which acts as site for charging[11] as a result of adsorption of the benzoheteroazepines. Inhibition efficiency calculated from the R_t values of mild steel in 1M H_2SO_4 with and without various concentrations of the compounds follows the same trend as that obtained from weight loss and polarization techniques.

5.5 Potentiodynamic polarization studies

Figures (5.21-5.32) show the cathodic and anodic polarization curves of mild steel in 1M H_2SO_4 with selected concentrations of the heteroazepines. It is observed that compared to blank, the cathodic curves show lower current density in the presence of benzoxazepines, while both anodic and cathodic curves show lower current density in presence of benzothiazepines. The cathodic curves show lower current density at all concentration and at higher concentration the current density was decreased in the anodic region also in presence of the benzodiazepines. The Tafel curves are shifted towards slightly less negative potential in the case of benzothiazepines. The curves are shifted to more negative potential for benzoxazepines, but for benzodiazepines a mixed behavior was noted. The corrosion potential E_{corr}, corrosion current density I_{corr} and the cathodic and anodic Tafel slopes (b_c and b_a) derived from the polarization plots are recorded in Table (5.19 - 5.21). Inspection of the data shows that in the presence of benzothiazepines E_{corr} values are shifted from -480 mV in blank 1M H_2SO_4 to slightly less negative potential with a maximum shift of 40 mV for 200 ppm of TMBTZ while in the presence of benzoxazepines shift in the more negative cathodic domain was observed. Compared to -480 mV for free 1M H_2SO_4, maximum shift of 60 mV was observed with 200 ppm of diphenylmethylbenzoxazepine (DPBOZ). In the case of benzodiazepines, presence of EPBD shifts the E_{corr} to slightly less negative values showing slight anodic behavior and other three compounds display mixed behavior[12]. Both b_a and b_c values are changed in the presence of the compounds, with benzothiazepines affecting anodic slope (b_a) more, compared to cathodic slope (b_c).

The percentage inhibition efficiency was calculated using the corrosion current density.

$$IE(\%) = \frac{I_{corr(blank)} - I_{corr(inh)}}{I_{corr(blank)}} \times 100$$

In general inhibition efficiency increased with concentration and same order of efficiency as obtained by weight loss method was observed in polarization measurements also. It can be concluded from polarization data that all the three sets of inhibitors are mixed type but the benzothiazepines are slightly anodic signifying that suppression of anodic metal dissolution is also possible. The benzoxazepines, benzodiazepines on the other hand are mixed type, inhibiting corrosion by minimizing anodic and cathodic corrosion reactions.

5.6 SEM and EDX spectra

The surface of mild steel specimen was examined under scanning electron microscope after immersion in blank acid (1M H_2SO_4) and inhibited acid (1M H_2SO_4+ 200 ppm EPBTZ) and the micrographs are shown in Figure 5.33a - 5.33e. From the figures it is evident that the surface of the mild steel was heavily corroded in blank acid (1M H_2SO_4) whereas in presence of the benzothiazepine it is smoother, means that the corrosion of mild steel is reduced by the adsorbed layer of the inhibitor. EDX spectra of mild steel specimen immersed in 1M H_2SO_4 containing DPBTZ (Figure 5.34a - 5.34d) shows a large peak due to sulphur confirming the presence of adsorbed inhibitor molecule on the steel surface. The data are presented in Table 5.22 -5.24.

5.7 Comparison of inhibition performance of benzothiazepines, benzoxazepines and benzodiazepines

In this chapter, the corrosion inhibition performance of benzothiazepines, benzoxazepines and benzodiazepines for mild steel in 1M H_2SO_4 has been analyzed. In each type four compounds have been chosen and compared. Results obtained by all the three methods indicated that the benzothiazepines are excellent inhibitors under all the experimental conditions. Substituents influenced the inhibition efficiency of the benzothiazepines and benzoxazepines in the same way as observed for benzodiazepines (chapter 4).

The following observations were made from the experimental studies:

- The benzothiazepines exhibited > 80% efficiency at 200 ppm, when compared with benzoxazepines and benzodiazepines.

- Benzothiazepines exhibit maximum value of free energy of adsorption (-37.38 kJ/mol) whereas benzoxazepines and benzodiazepines shows slightly lower values of -33 kJ/mol and -35 kJ/mol.
- E_{corr} value is shifted to less negative direction for benzothiazepines. Benzodiazepines and benzoxazepines shifted the E_{corr} to slightly more negative direction.
- I_{corr} value of mild steel is reduced to a maximum extent in the presence of 200 ppm of EPBTZ (414 μ A/cm^2 to 60 μ A /cm^2) whereas the analogous benzoxazepine EPBOZ reduced the I_{corr} of steel from 414 μ A /cm^2 to 112 μ A/cm^2. With benzodiazepine the current density is reduced from 414 μ A/cm^2 to 53 μ A /cm^2.
- Anodic Tafel slope b_a is affected more in presence of benzothiazepines.
- Decrease in double layer capacitance (C_{dl}) and increase in charge transfer resistance (R_t) for mild steel in 1M H_2SO_4 are more in presence of benzothiazepines compared to diazepines or oxazepines.

These observations suggest that the adsorption and inhibition of benzothiazepines are different from that of diazepines or oxazepines, which can be explained as follows.

The adsorption of organic molecules on solid surfaces cannot be considered as purely physical or chemical adsorption phenomenon. Molecules containing nitrogen atom get protonated in acid medium. The protonated organic cations get adsorbed via electrostatic attraction by SO_4^{2-} anions which are adsorbed on positively charged iron ions on the mild steel surface in acid medium. The free energy of adsorption value is around - 20 kJ/mol. On the other hand chemisorption takes place more slowly than electrostatic adsorption and with higher activation energy[13]. It depends on temperature and is specific for certain metals. Electron transfer can be expected with compounds having relatively loosely bound electrons. Mahmoud *et al.,* [14] have reported that sulphur compounds are better corrosion inhibitors than their nitrogen or oxygen analogues because S atom is less electronegative than N or O and being thus more efficient electron donor forming chemisorptive bond. Loto *et al.,* [15] have opined that sulphur is easily protonated in acid solution and is also a stronger electron donor than nitrogen. Hence sulphur compounds get protonated and adsorbed electrostatically at lower concentration. At higher concentrations, the electron rich S centers of unprotonated molecules get adsorbed on the anodic sites via chemisorption.

HSAB principle has been applied by many authors to explain adsorption bond strength and inhibition. According to hard and soft acid base principle, hard acids prefer to coordinate with hard base; soft acids prefer to bind to soft base[16, 17, 18]. Metal atoms on oxide free surfaces are considered as soft acids which in acid solution form stronger bonds with soft bases such as sulphur compounds and O containing inhibitors are hard bases and establish weaker bonds with metal surfaces in acid solution.

The positive shift in the corrosion potential due to benzothiazepines (Table 5.19) showed that these compounds are effective suppressors of anodic dissolution reaction. The cathodic polarization curves in Figure (5.15-5.22) show that these compounds also reduce cathodic hydrogen evolution. Benzodiazepines and benzoxazepines shift the E_{corr} to more negative direction and thus they essentially suppress cathodic hydrogen evolution.

The ΔG°_{ads} values also suggest a mixed adsorption mode by benzothiazepines. The values approach to -40 kJ/mol which is the threshold value for chemisorption type bond. Hence it can be concluded that benzothiazepines get adsorbed more at cathodic and anodic sites on steel surface and inhibit corrosion more effectively than benzodiazepines or benzoxazepines.

References

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Tables

Table 5.1 Molecular structure of benzothiazepines

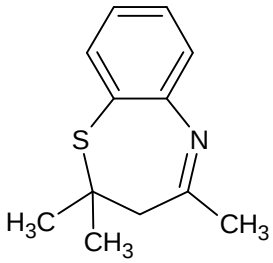
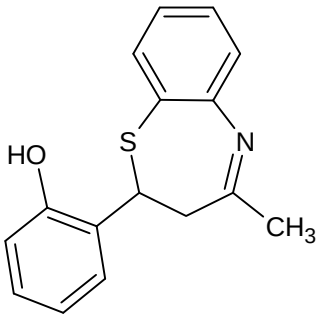
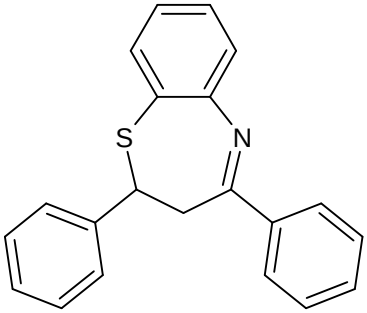
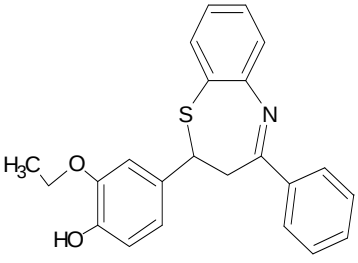
Structure	IUPAC Nomenclature	Abbreviation	Melting point (°C)
	2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzothiazepine	TMBTZ	122
	2-(2-Hydroxyphenyl)-4-methyl-2,3-dihydro-1*H*-1,5-benzothiazepine	MBTZ	80
	2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzothiazepine	DPBTZ	113-117
	2-(3-ethoxy-4-hydroxyphenyl)-4-phenyl-2,3-dihydro-1*H*-benzothiazepine	EPBTZ	175

Table 5.2 Molecular structure of benzoxazepines

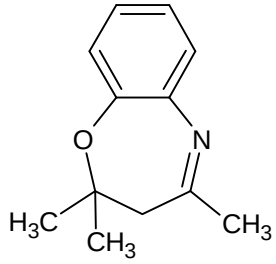
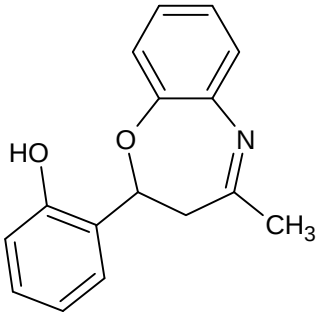
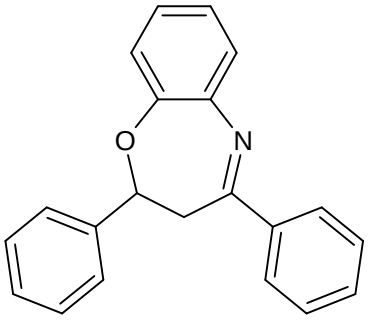
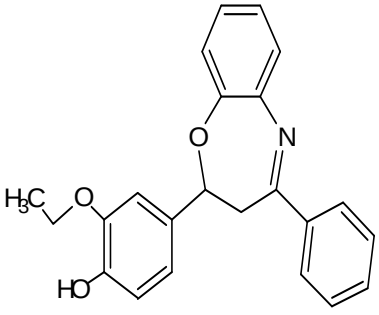
Structure	IUPAC Nomenclature	Abbreviation	Melting Point (°C)
	2,2,4-trimethyl-2,3-dihydro-1,5-1*H*-benzoxazepine	TMBOZ	102
	2-(2-Hydroxyphenyl)-4-methyl-2,3-dihydro-1*H*-1,5-benzoxazepine	MBOZ	118
	2,4-diphenyl-2,3-dihydro-1,5-1*H*-benzoxazepine	DPBOZ	110
	2-(3-ethoxy-4-hydroxyphenyl)-4-phenyl-2,3-dihydro-1*H*-benzoxazepine	EPBOZ	108

Table 5.3 Molecular structure of benzodiazepines

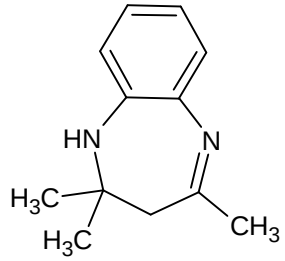
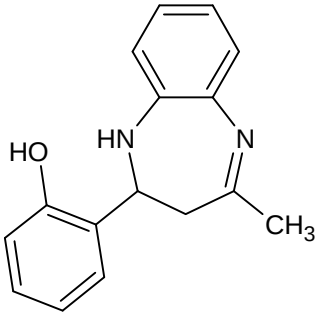
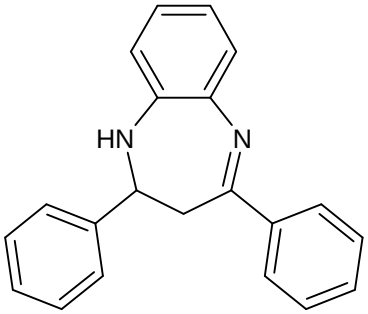
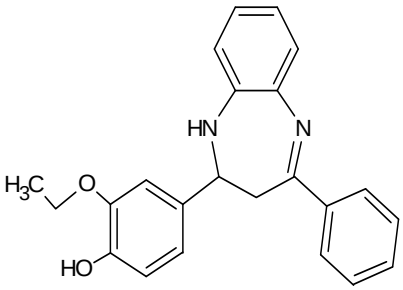
Structure	IUPAC Nomenclature	Abbreviation	Melting Point (°C)
	2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine	TMBD	126
	2-(2-hydroxyphenyl)-4-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine	MBD	110
	2,4-diphenyl-2,3-dihydro-1*H*-1,5-1*H*-benzodiazepine	DPBD	136-137
	2-(3-ethoxy-4-hydroxyphenyl)-2-phenyl-2,3-dihydro-1*H*-1,5-benzodiazepine	EPBD	122-124

Table 5.4 Inhibition efficiencies of various concentrations of benzothiazepines for corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurements at 303 ± 1K

Name of the inhibitor	Concentration(ppm)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
BLANK	-	0.2656	-	-	17466.71
TMBTZ	10	0.1339	49.58	0.4958	8805.69
	50	0.1181	55.58	0.5558	7766.63
	100	0.0986	62.87	0.6287	6484.25
	150	0.0800	69.87	0.6987	5261.05
	200	0.0684	74.24	0.7424	4498.20
MBTZ	10	0.1133	57.34	0.5734	7450.97
	50	0.0965	63.66	0.6366	6346.15
	100	0.086	67.62	0.6762	7450.97
	150	0.0626	76.43	0.7643	4116.77
	200	0.0279	89.49	0.8949	1834.79
DPBTZ	10	0.1319	50.33	0.5033	8674.16
	50	0.1139	57.11	0.5711	7490.43
	100	0.0945	64.42	0.6442	6214.62
	150	0.0754	71.61	0.7161	4954.54
	200	0.0378	85.76	0.8576	2485.85
EPBTZ	10	0.089	66.49	0.6649	5852.92
	50	0.0769	71.04	0.7104	5057.19
	100	0.056	78.91	0.7891	3682.74
	150	0.0478	82.00	0.8200	3143.48
	200	0.0177	93.33	0.9333	1164.00

Table 5.5 Inhibition efficiencies of various concentrations of benzoxazepines for corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurements at $303 \pm 1K$

Name of the inhibitor	Concentration (ppm)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
BLANK	-	0.2656	-	-	17466.71
TMBOZ	10	0.1564	41.11	0.4111	10285.37
	50	0.1453	45.29	0.4529	9555.39
	100	0.1265	52.37	0.5237	8319.04
	150	0.1065	59.90	0.5990	70003.78
	200	0.0987	62.83	0.6283	6490.83
MBOZ	10	0.1392	47.59	0.4759	9154.24
	50	0.1267	52.29	0.5229	8332.2
	100	0.0987	62.83	0.6283	6490.83
	150	0.0652	75.45	0.7545	4287.76
	200	0.0504	81.02	0.8102	3314.46
DPBOZ	10	0.1233	53.57	0.5357	8108.60
	50	0.0914	65.58	0.6558	6010.75
	100	0.0731	72.47	0.7247	4807.29
	150	0.0633	76.16	0.7616	4162.81
	200	0.0448	83.13	0.8313	2946.19
EPBOZ	10	0.1082	59.26	0.5926	7115.58
	50	0.0756	71.53	0.7153	4971.7
	100	0.0687	74.13	0.7413	4517.93
	150	0.0377	85.80	0.8580	2479.27
	200	0.036	86.44	0.8644	2367.47

Table 5.6 Inhibition efficiencies of various concentrations of benzodiazepines for corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurements at 303 ± 1K

Name of the inhibitor	Concentration (ppm)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
BLANK	-	0.2656	-	-	17466.71
TMBD	10	0.1532	42.31	0.4231	10074.9
	50	0.1414	46.76	0.4676	9298.92
	100	0.1198	54.89	0.5489	7878.43
	150	0.1022	61.52	0.6152	6721.00
	200	0.092	65.36	0.6536	6037.06
MBD	10	0.0928	65.06	0.6506	6102.82
	50	0.0775	70.82	0.7082	5096.65
	100	0.0665	74.96	0.7496	4373.19
	150	0.0566	78.68	0.7868	3722.19
	200	0.0513	80.68	0.8068	3373.65
DPBD	10	0.1185	55.38	0.5538	7792.94
	50	0.0986	62.87	0.6287	6484.25
	100	0.0865	67.43	0.6743	5688.51
	150	0.0765	71.19	0.7119	5030.88
	200	0.06	77.40	0.7740	3945.79
EPBD	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

Table 5.7 Corrosion parameters for mild steel in 1M H_2SO_4 in the absence and presence of different concentrations of benzothiazepines at different temperature.

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
TMBTZ	303	0.0228	74.23	0.7423	4498.17
	313	0.0415	63.97	0.6397	8187.46
	323	0.069	52.18	0.5218	13612.9
	333	0.1318	46.98	0.4698	26002.6
MBTZ	303	0.0093	89.49	0.8949	1834.78
	313	0.0258	77.60	0.7760	5090.04
	323	0.0486	66.32	0.6632	9588.21
	333	0.1005	59.57	0.5957	19827.5
DPBTZ	303	0.0126	85.76	0.8576	2485.83
	313	0.0295	74.39	0.7439	5820.0
	323	0.0573	60.29	0.6029	11304.6
	333	0.1185	52.33	0.5233	23378.7
EPBTZ	303	0.0059	93.33	0.9333	1164.0
	313	0.0163	85.85	0.8585	3215.8
	323	0.035	75.74	0.7574	6905.09
	333	0.0858	65.48	0.6548	16927.3

Table 5.8 Corrosion parameters for mild steel in 1M H_2SO_4 in the absence and presence of different concentrations of benzoxazepines at different temperature.

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
TMBOZ	303	0.0329	62.82	0.6282	6490.83
	313	0.0522	54.68	0.5468	10298.44
	323	0.0842	41.64	0.4164	16611.67
	333	0.1563	37.12	0.3712	30836.15
MBOZ	303	0.0168	81.01	0.8101	3314.46
	313	0.0345	70.05	0.7005	6806.44
	323	0.0535	62.92	0.6292	10554.92
	333	0.1125	54.74	0.5474	22194.92
DPBOZ	303	0.0149	83.16	0.8316	2939.61
	313	0.0386	66.49	0.6649	7615.32
	323	0.0596	58.69	0.5869	11758.38
	333	0.1256	49.47	0.4947	24779.4
EPBOZ	303	0.012	86.44	0.8644	2367.47
	313	0.0292	74.65	0.7465	5760.81
	323	0.0514	64.37	0.6437	10140.61
	333	0.102	58.97	0.5897	20123.4

Table 5.9 Corrosion parameters for mild steel in 1M H_2SO_4 in the absence and presence of different concentrations of benzodiazepines at different temperature.

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition efficiency (%)	Degree of Surface coverage (θ)	Corrosion rate (mpy)
TMBD	303	0.0306	65.42	0.6542	6037.01
	313	0.0546	52.60	0.5260	10771.94
	323	0.0846	41.37	0.4137	16690.58
	333	0.1683	32.30	0.3230	33203.61
EPBD	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
DPBD	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
MBD	303	0.0171	80.67	0.8067	3373.62
	313	0.034	70.48	0.7048	6707.79
	323	0.056	61.19	0.6119	11048.14
	333	0.1084	56.39	0.5639	21386.04

Table 5.10 Thermodynamic parameters for the corrosion of mild steel in 1M H_2SO_4 at 200 ppm concentration of the benzothiazepines

Name of the inhibitor	E_a (kJ/mol)	ΔG^*(kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (kJ K^{-1} mol^{-1})
BLANK	27.7	-21.56	25.18	0.15
TMBTZ	48.37	-23.05	45.85	0.22
DPBTZ	62.42	-23.70	59.90	0.27
MBTZ	65.95	-24.03	63.45	0.28
EPBTZ	73.81	-22.49	71.29	0.30

Table 5.11 Thermodynamic parameters for the corrosion of mild steel in 1M H_2SO_4 at 200 ppm concentration of the benzoxazepines

Name of the inhibitor	E_a (kJ/mol)	ΔG^* (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (kJ K^{-1} mol^{-1})
BLANK	27.7	-21.56	25.18	0.15
TMBOZ	37.25	-20.86	34.73	0.18
DPBOZ	40.60	-22.62	38.08	0.20
MBOZ	45.31	-22.83	42.79	0.22
EPBOZ	48.31	-23.08	45.79	0.23

Table 5.12 Thermodynamic parameters for the corrosion of mild steel in 1M H_2SO_4 at 200 ppm concentration of the benzodiazepines

Name of the inhibitor	E_a (kJ/mol)	ΔG^* (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (kJ mol^{-1} K^{-1})
BLANK	27.7	-21.56	25.18	0.15
TMBD	39.95	-22.42	37.43	0.19
DPBD	40.40	-22.78	37.88	0.20
MBD	48.24	-23.07	45.72	0.22
EPBD	51.99	-23.53	49.47	0.24

Table 5.13 Langmuir adsorption isotherm parameters for benzothiazepines at 303 ± 1K

Compound	K_{ads} (M^{-1}) X 10^4	R^2	$-\Delta G^{o}_{ads}$ (kJ/mol)
TMBTZ	1.42	0.9959	34.20
MBTZ	2.5	0.9948	35.63
DPBTZ	5	0.9974	37.38
EPBTZ	5	0.9989	37.38

Table 5.14 Langmuir adsorption isotherm parameters for benzoxazepines at 303±1K

Compound	K_{ads} (M^{-1}) X 10^4	R^2	$-\Delta G^{\circ}_{ads}$ (kJ/mol)
TMBOZ	1	0.9876	33.32
MBOZ	1	0.9792	33.32
DPBOZ	2	0.9932	35.07
EPBOZ	1.6	0.9946	34.51

Table 5.15 Langmuir adsorption isotherm parameters for benzodiazepines at 303±1K

Compound	K_{ads} (M^{-1}) X 10^4	R^2	$-\Delta G^{\circ}_{ads}$ (kJ/mol)
TMBD	1.11	0.9945	33.58
MBD	1.42	0.9993	34.20
DPBD	2.5	0.993	35.63
EPBD	3.3	0.993	36.33

Table 5.16 Impedance parameters for the corrosion of mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepines at 303 ± 1K.

Name of the inhibitor	Concentration (ppm)	R_t (ohm.cm^2)	C_{dl} (µF/cm^2)	Inhibition efficiency (%)
BLANK	-	18.00	38.80	-
TMBTZ	10	48.00	20.59	62.50
	100	50.00	19.62	64.00
	200	54.00	15.77	66.66
EPBTZ	10	79.00	18.32	77.21
	100	80.00	16.78	77.50
	200	89.00	15.02	79.77
DPBTZ	10	51.00	16.62	64.70
	100	59.00	16.21	69.49
	200	80.00	14.32	77.50
MBTZ	10	61.00	20.41	70.49
	100	70.00	19.54	73.91
	200	89.00	18.17	79.88

Table 5.17 Impedance parameters for the corrosion of mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepines at 303±1K.

Name of the inhibitor	Concentration (ppm)	R_t (ohm.cm^2)	C_{dl} (µF/cm^2)	Inhibition efficiency (%)
BLANK	-	18.00	38.80	-
EPBOZ	10	25.00	19.16	28.00
	100	37.00	18.72	51.35
	200	54.00	15.32	66.66
MBOZ	10	22.00	20.35	18.18
	100	30.00	18.11	40.00
	200	34.00	17.445	47.05
DPBOZ	10	21.00	17.28	14.20
	100	27.00	23.19	33.33
	200	31.00	22.53	41.93
TMBOZ	10	20.5	18.43	12.19
	100	27.3	16.56	34.06
	200	33.00	15.23	45.45

Table 5.18 Impedance parameters for the corrosion of mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepines at 303±1K.

Name of the inhibitor	Concentration (ppm)	R_t (ohm.cm^2)	C_{dl} (µF/cm^2)	Inhibition efficiency (%)
BLANK	-	18.00	38.80	-
TMBD	10	35.00	31.1	48.57
	100	45.00	30.8	60.00
	200	60.00	24.9	70.00
EPBD	10	60.00	30.8	70.00
	100	78.00	24.4	76.92
	200	120.00	19.7	85.00
DPBD	10	50.00	31.0	64.00
	100	78.00	29.7	76.92
	200	90.00	29.5	80.00
MBD	10	52.00	29.5	65.38
	100	65.00	22.7	72.30
	200	115.00	19.7	84.34

Table 5.19 Corrosion parameters for corrosion of mild steel in 1M H_2SO_4 with selected concentrations of benzothiazepines by potentiodynamic polarization method at 303 ± 1K

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Inhibition efficiency (%)
		b_a	$-b_c$			
BLANK	-	68	167	-480	414	-
TMBTZ	10	54	124	-460	233	43.71
	100	52	125	-450	181	56.28
	200	50	128	-440	161	61.11
EPBTZ	10	47	139	-444	168	59.42
	100	43	138	-443	105	74.63
	200	41	138	-442	60	85.50
DPBTZ	10	48	126	-444	187	54.83
	100	40	151	-445	165	68.59
	200	42	145	-446	80	80.67
MBTZ	10	61	124	-478	220	46.85
	100	47	144	-430	105	74.63
	200	48	148	-440	92	77.77

Table 5.20 Corrosion parameters for corrosion of mild steel in 1M H_2SO_4 with selected concentrations of benzoxazepines by potentiodynamic polarization method at 303 ± 1K.

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Inhibition efficiency (%)
		b_a	$-b_c$			
BLANK	-	61	137	-470	414	-
EPBOZ	10	52	106	-482	171	58.69
	100	65	132	-483	139	66.42
	200	56	128	-490	112	72.94
MBOZ	10	101	122	-490	188	54.58
	100	71	121	-485	156	62.31
	200	56	118	-498	133	67.87
DPBOZ	10	64	134	-510	252	39.13
	100	59	128	-520	216	47.82
	200	54	126	-530	137	66.90
TMBOZ	10	62	122	-482	256	38.16
	100	58	114	-490	235	45.65
	200	65	135	-480	142	65.70

Table 5.21 Corrosion parameters for corrosion of mild steel in 1M H_2SO_4 with selected concentrations of benzodiazepines by potentiodynamic polarization method at 303±1K.

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Inhibition efficiency (%)
		b_a	$-b_c$			
BLANK	-	68	167	-480.0	414.0	-
TMBD	10	62	148	-490.0	280.00	32.36
	100	58	158	-485.0	240.60	41.88
	200	48	171	-460.0	170.00	58.93
MBD	10	64	155	-482.0	250.0	39.61
	100	57	135	-485.0	160.0	61.34
	200	47	142	-490.2	110.0	73.42
DPBD	10	60	173	-470.0	240.0	42.02
	100	58	164	-482.3	156.0	62.31
	200	52	167	-500.0	120.0	71.01
EPBD	10	62	159	-475.0	120.00	71.01
	100	56	157	-471.1	93.00	77.52
	200	48	163	-450.4	53.00	87.19

Table 5.22 EDX data for mild steel after 3 hours immersion in 1M H_2SO_4 in the presence and absence of 200 ppm DPBTZ

Name of the sample	Element	Weight (%)	Atomic weight (%)
BLANK	C	2.19	5.64
	O	28.38	54.92
	S	1.80	1.74
	Fe	66.78	37.02
DPBTZ	C	21.66	28.41
	O	68.08	67.05
	N	0.89	1.00
	S	4.27	2.10
	Fe	5.11	1.44

Table 5.23 EDX data for mild steel after 3 hours immersion in 1M H_2SO_4 in the presence and absence of 200 ppm DPBOZ

Name of the sample	Element	Weight (%)	Atomic weight (%)
BLANK	C	2.19	5.64
	O	28.38	54.92
	S	1.80	1.74
	Fe	66.78	37.02
DPBOZ	C	17.92	26.54
	O	58.05	64.55
	N	1.17	1.48
	S	0.30	0.17
	Fe	22.26	7.09

Table 5.24 EDX data for mild steel after 3 hours immersion in 1M H_2SO_4 in the presence and absence of 200 ppm DPBD

Name of the sample	Element	Weight (%)	Atomic weight (%)
BLANK	C	2.19	5.64
	O	28.38	54.92
	S	1.80	1.74
	Fe	66.78	37.02
DPBD	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

Figures

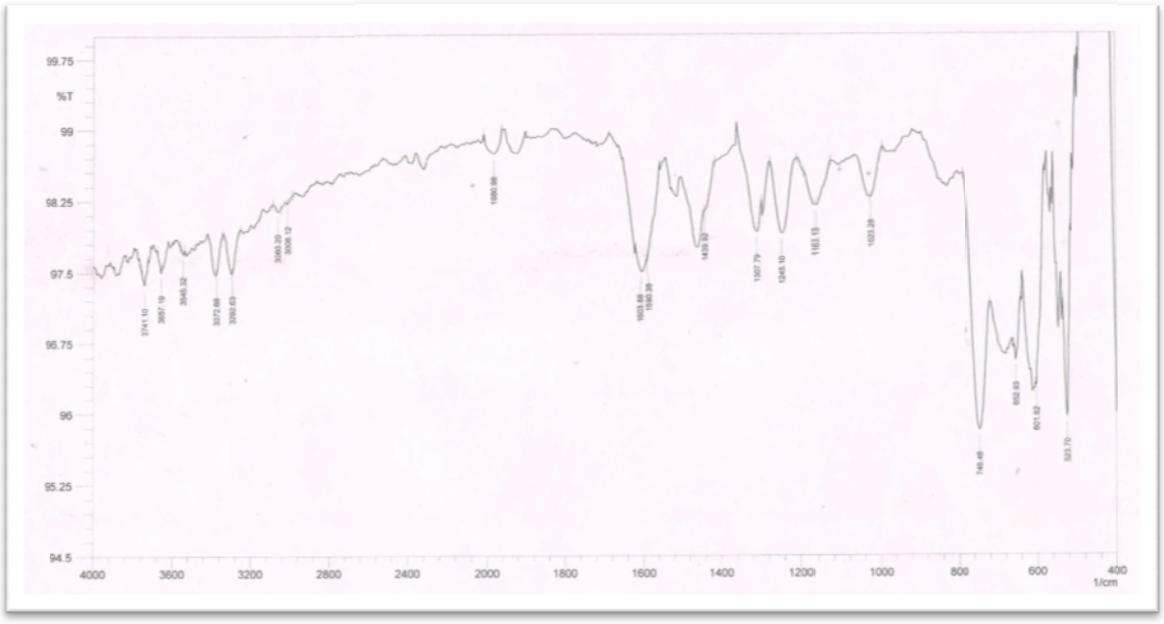


Figure 5.1 FTIR spectra of TMBTZ

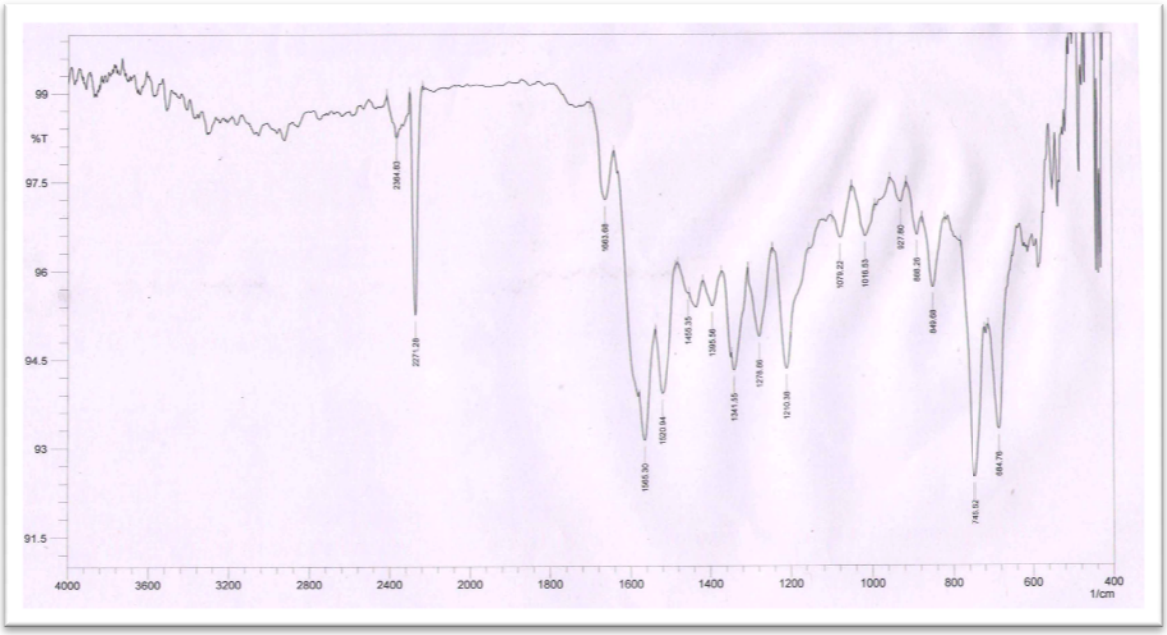


Figure 5.2 FTIR spectra of TMBOZ

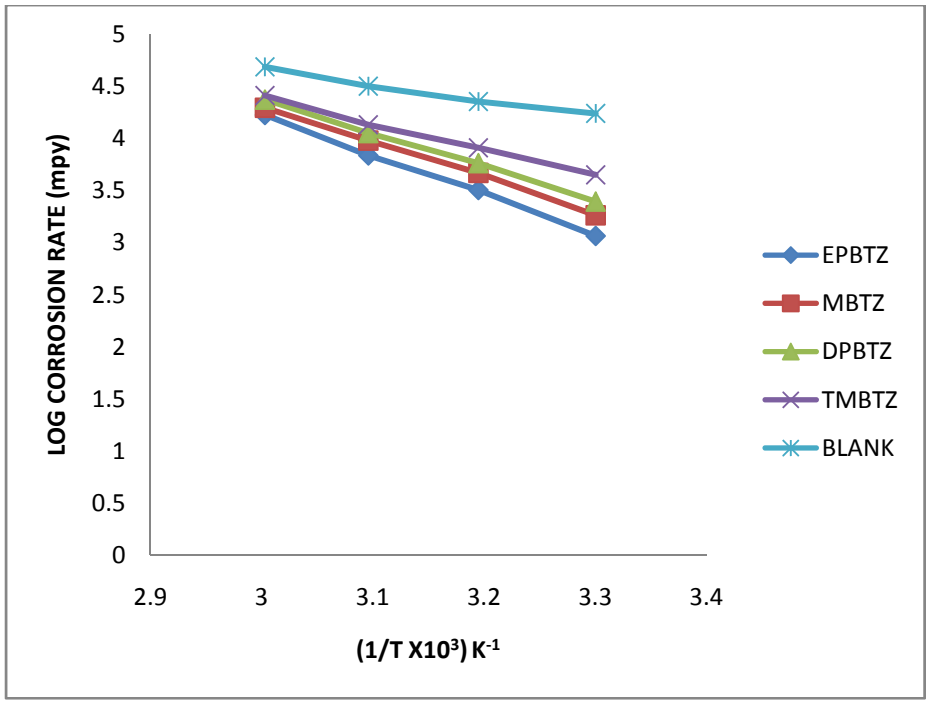


Figure 5.3 Arrhenius plots for mild steel in 1M H_2SO_4 with and without 200 ppm benzothiazepines

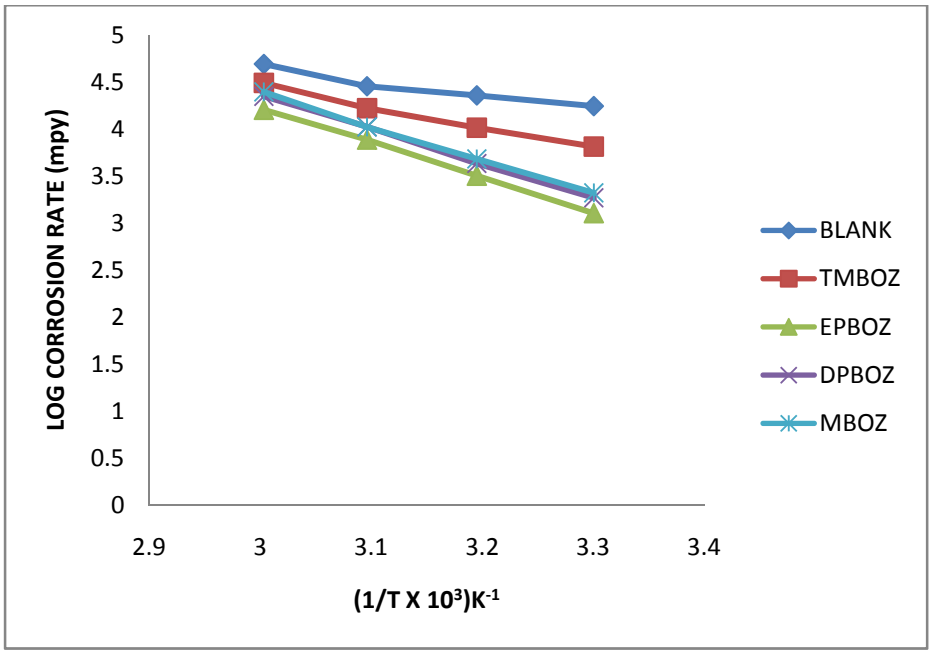


Figure 5.4 Arrhenius plots for mild steel in 1M H_2SO_4 without and with 200 ppm benzoxazepines

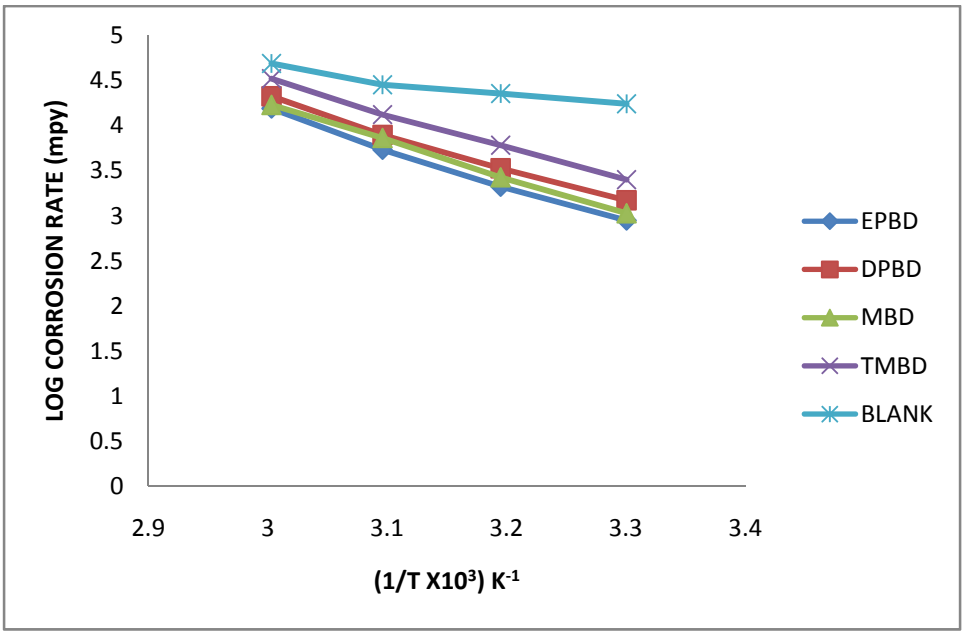


Figure 5.5 Arrhenius plots for mild steel in 1M H_2SO_4 without and with 200 ppm benzodiazepines

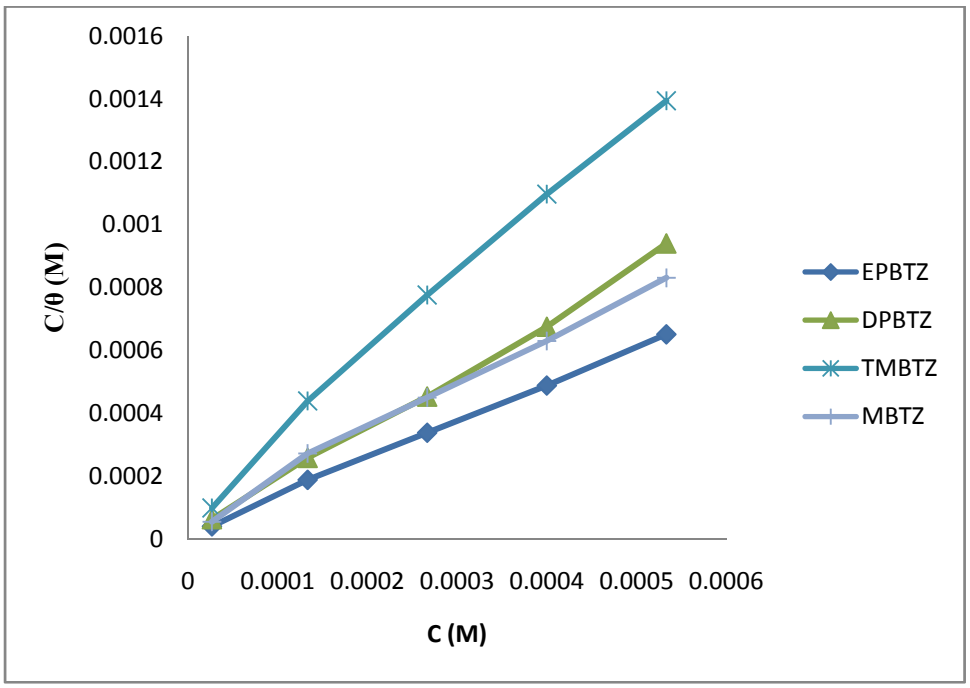


Figure 5.6 Langmuir plot for the benzothiazepines

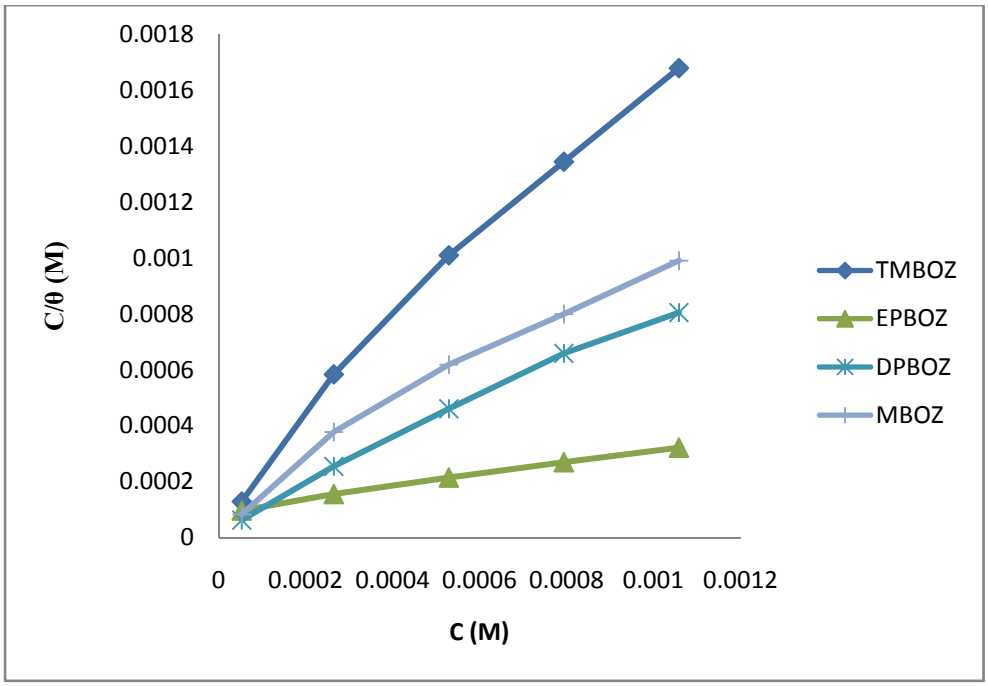


Figure 5.7 Langmuir plot for the benzoxazepines

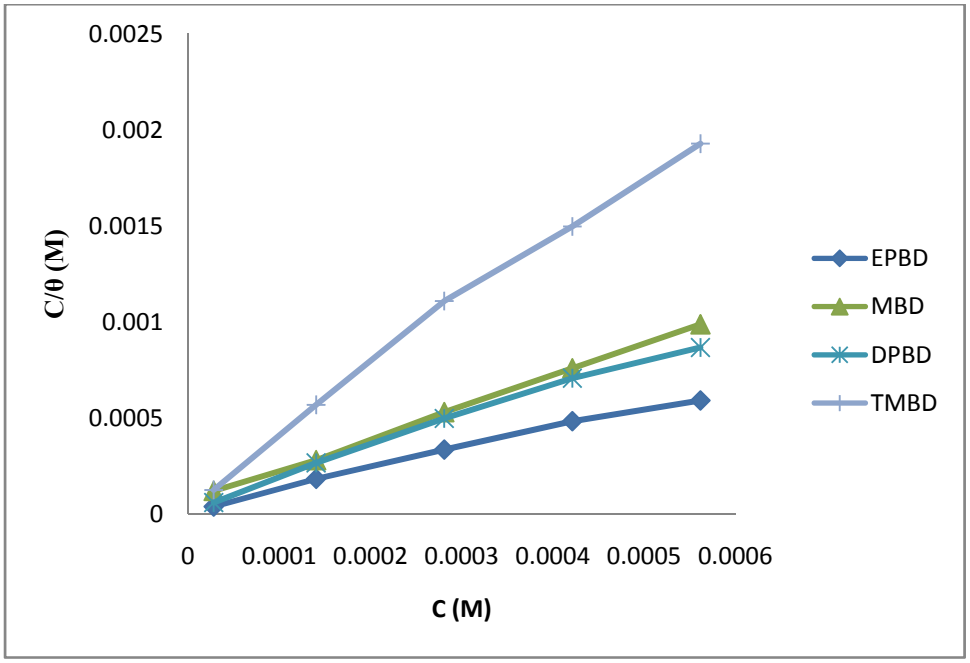


Figure 5.8 Langmuir plot for the benzodiazepines

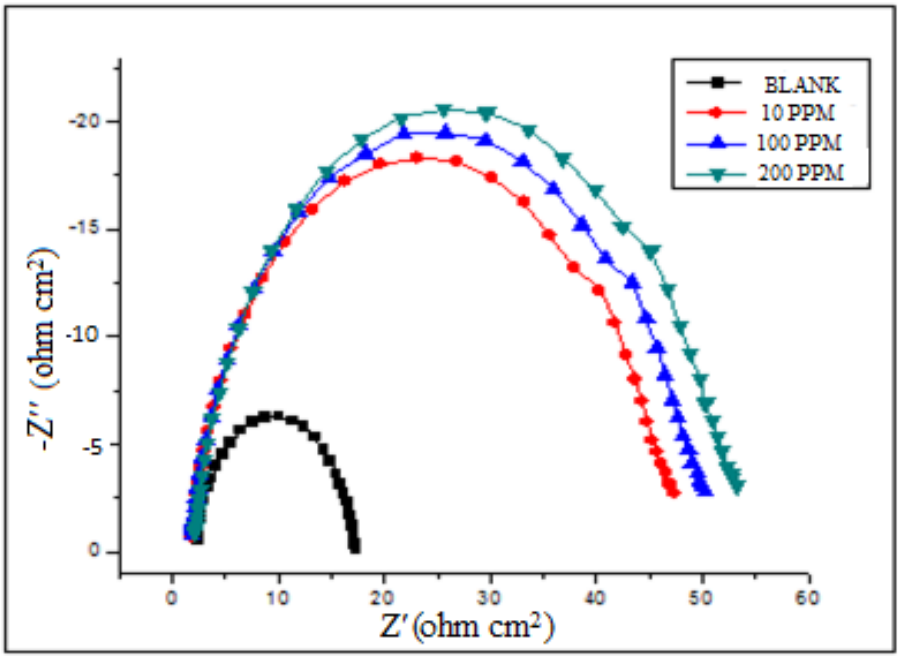


Figure 5.9 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine TMBTZ

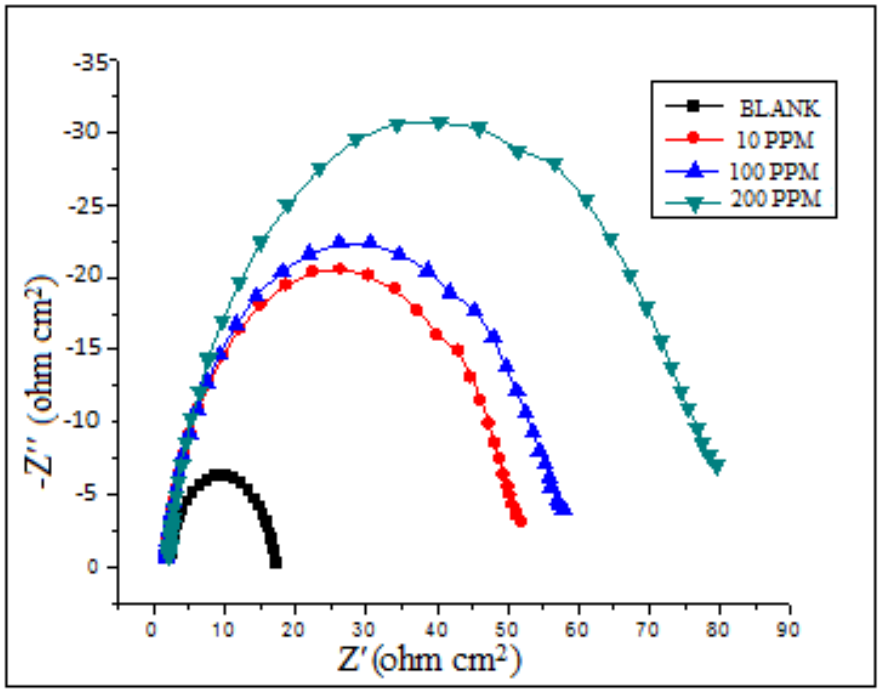


Figure 5.10 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine MBTZ

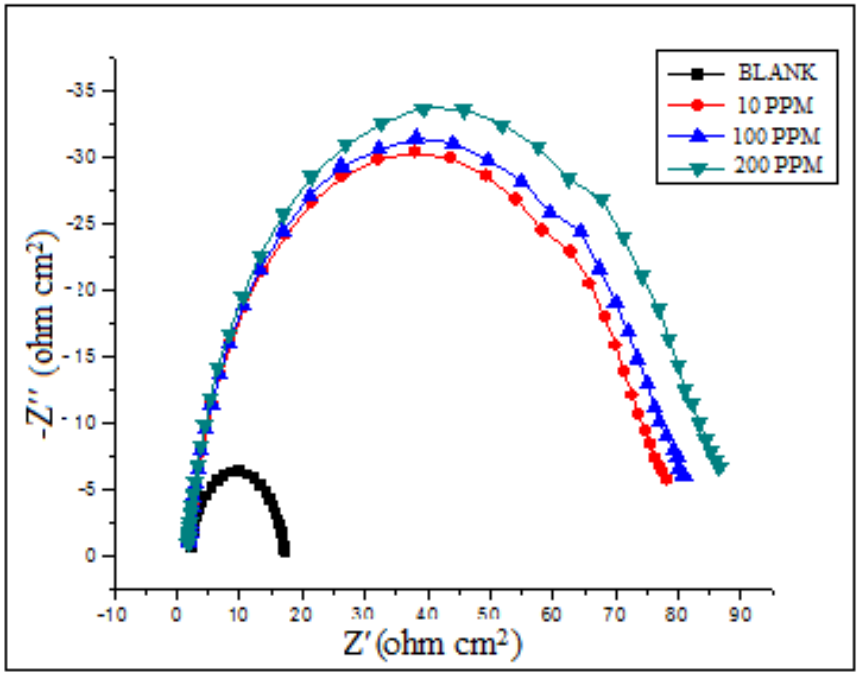


Figure 5.11 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine DPBTZ

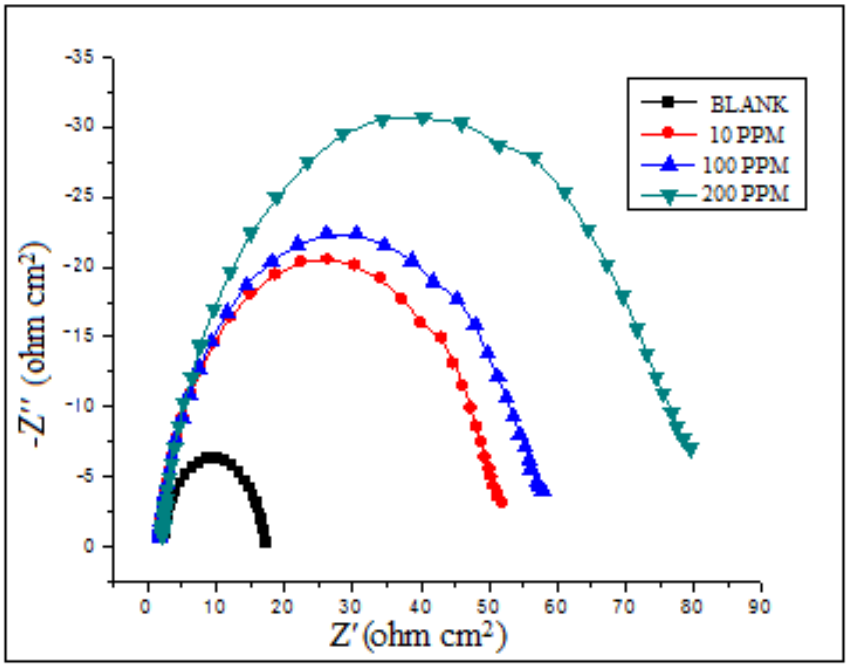


Figure 5.12 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine EPBTZ

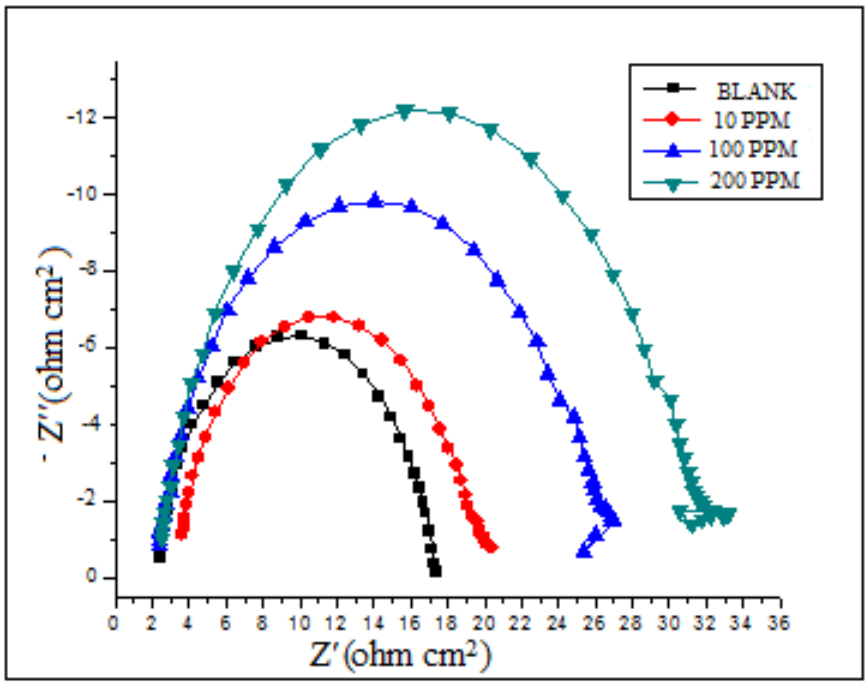


Figure 5.13 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine TMBOZ

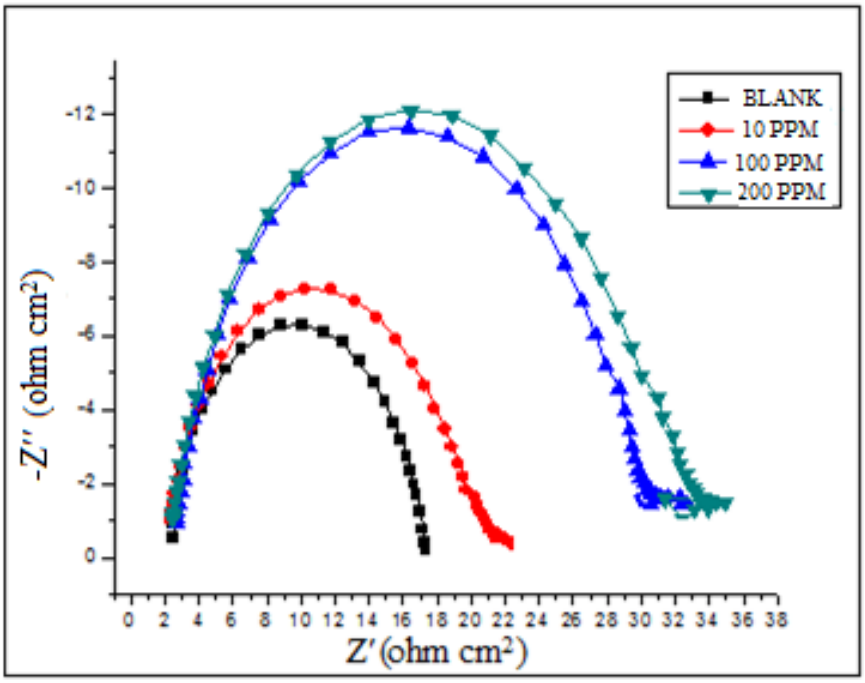


Figure 5.14 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine MBOZ

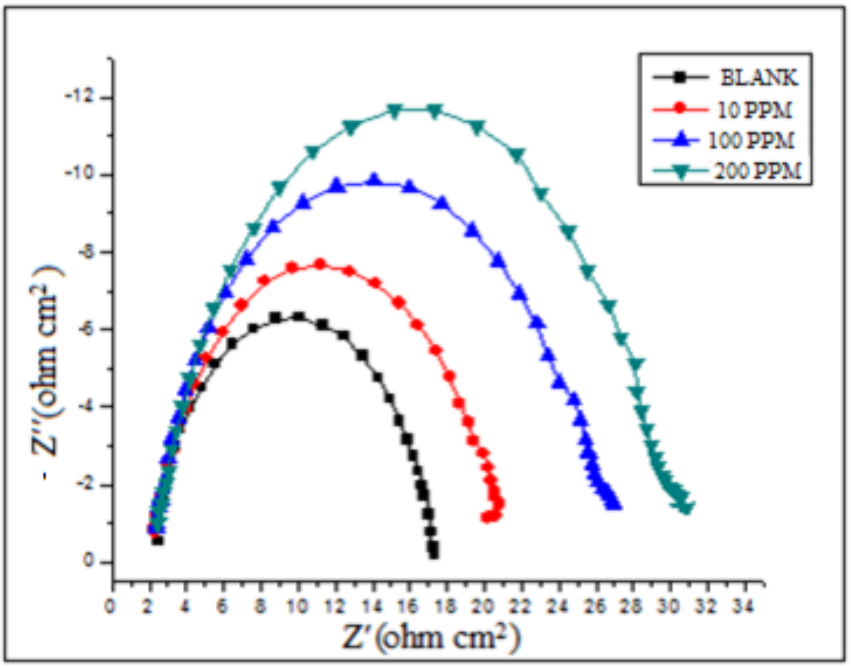


Figure 5.15 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine DPBOZ

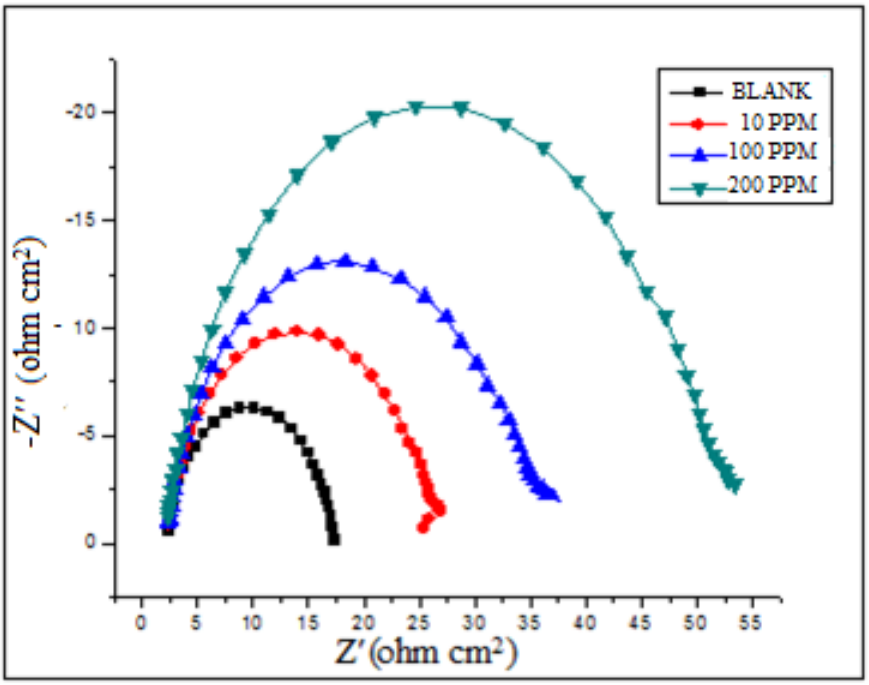


Figure 5.16 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine EPBOZ

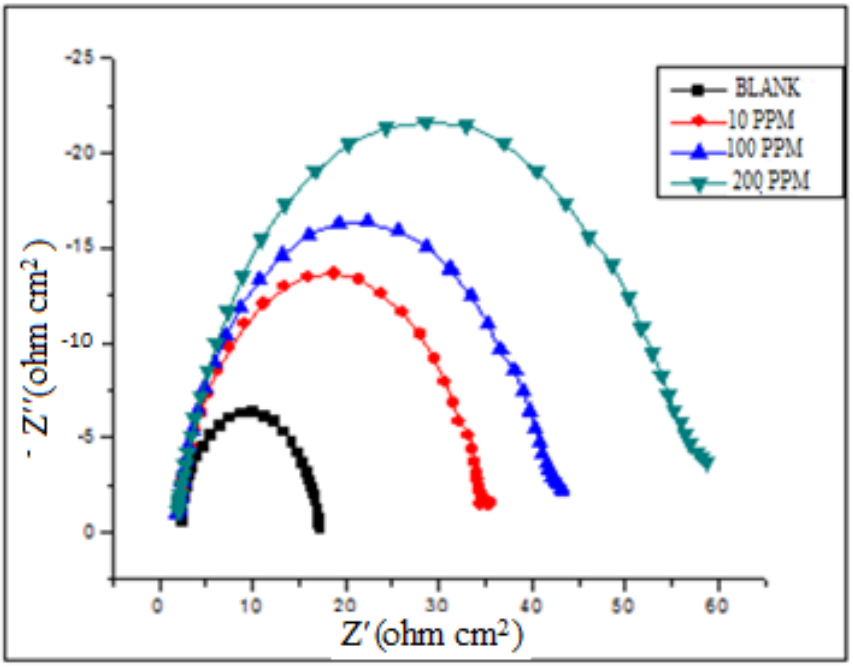


Figure 5.17 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine TMBD

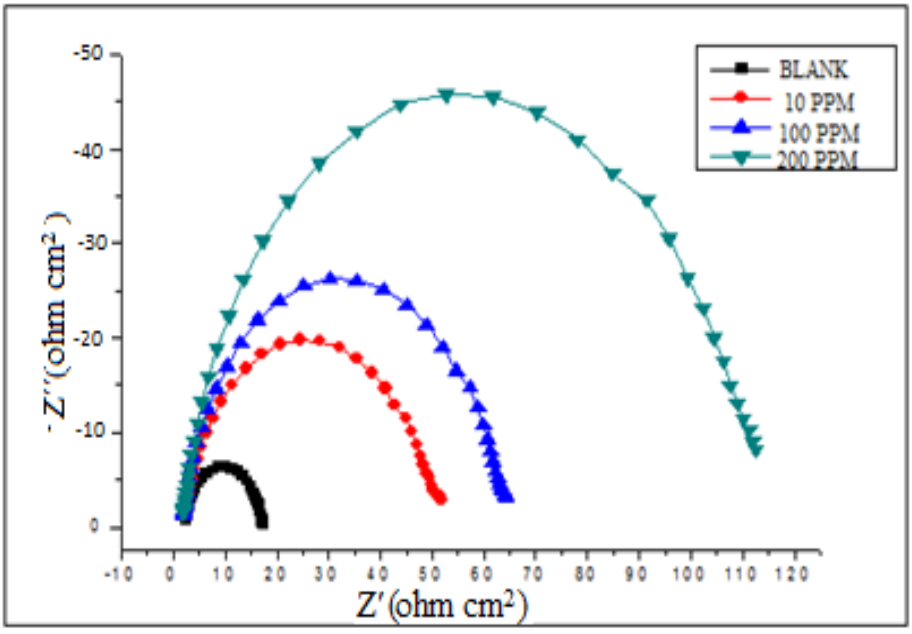


Figure 5.18 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine MBD

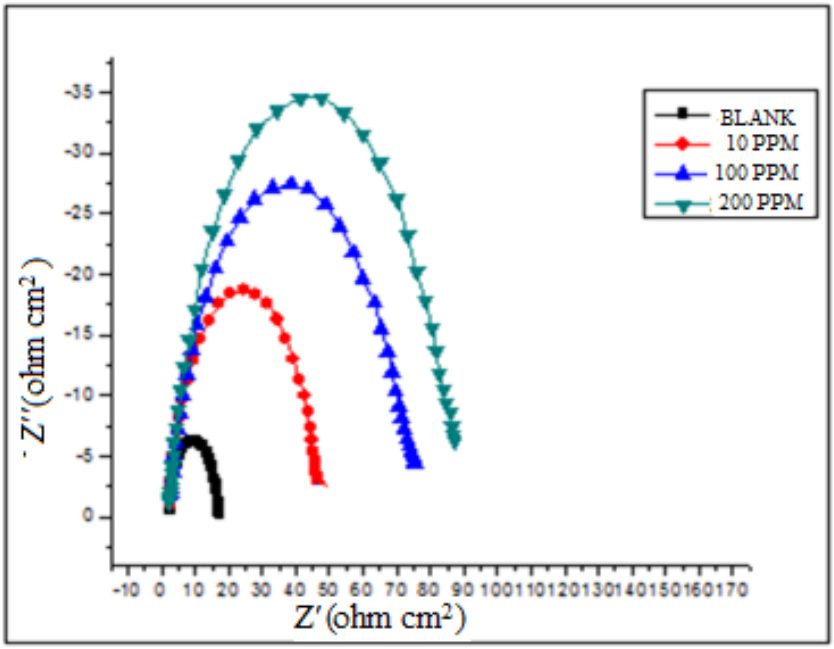


Figure 5.19 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine DPBD

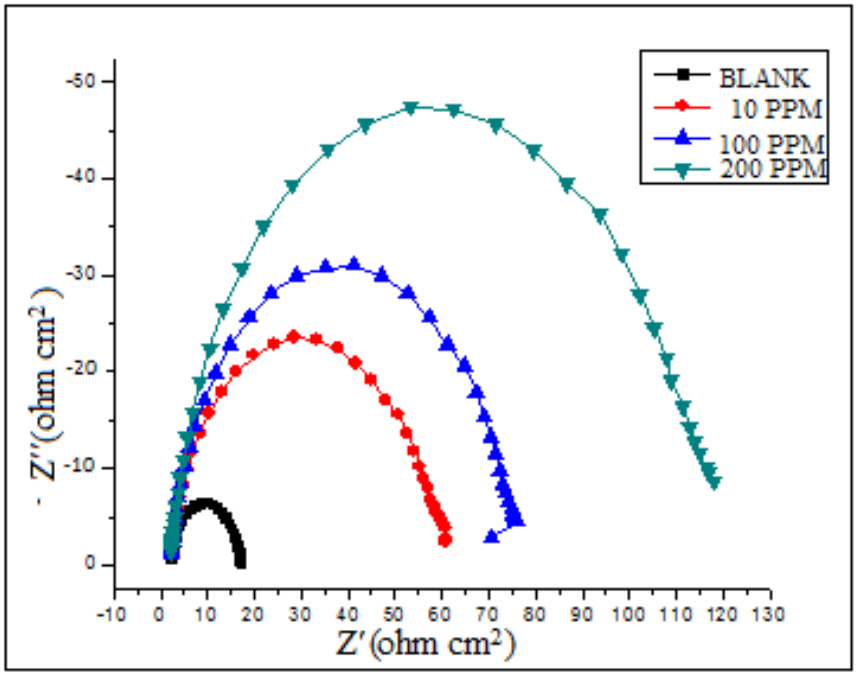


Figure 5.20 Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine EPBD

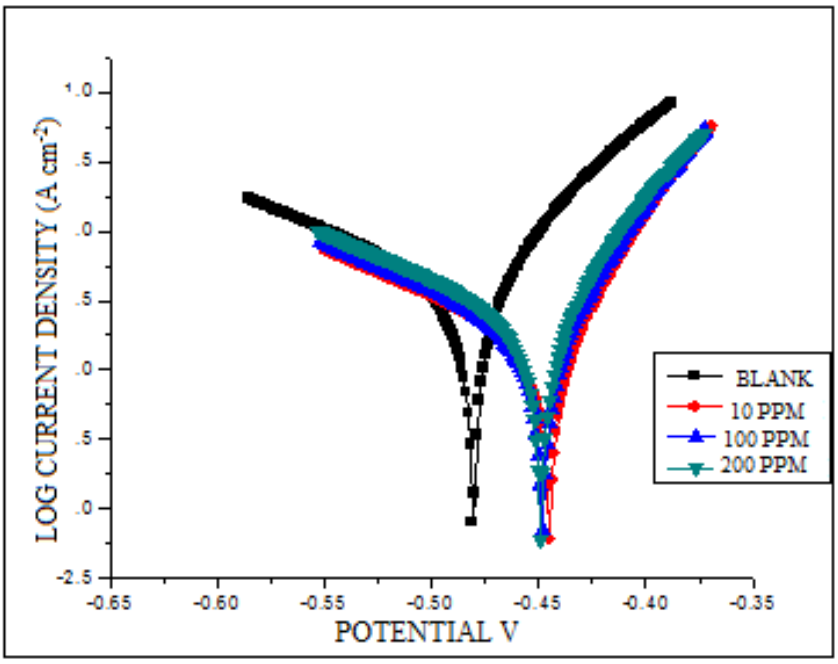


Figure 5.21 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine TMBTZ

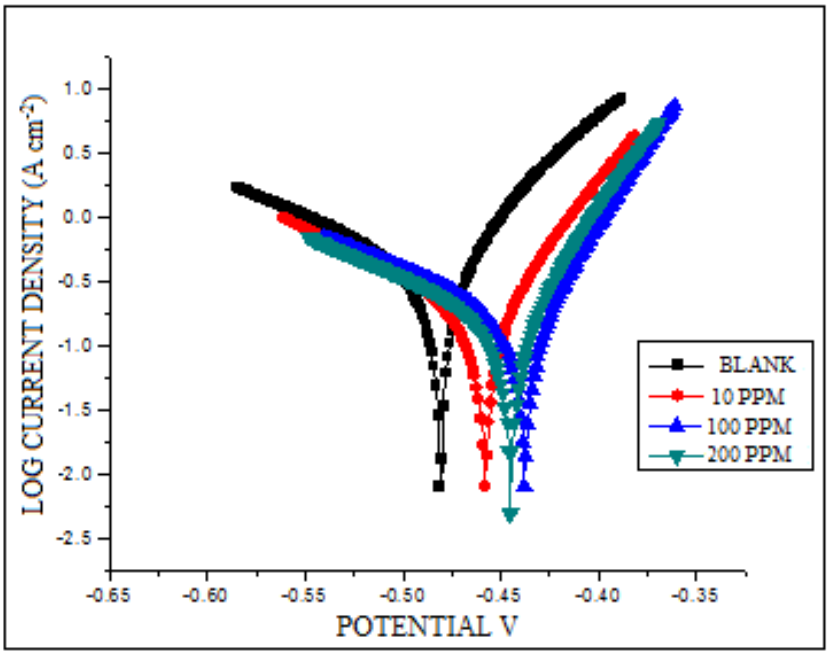


Figure 5.22 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine MBTZ

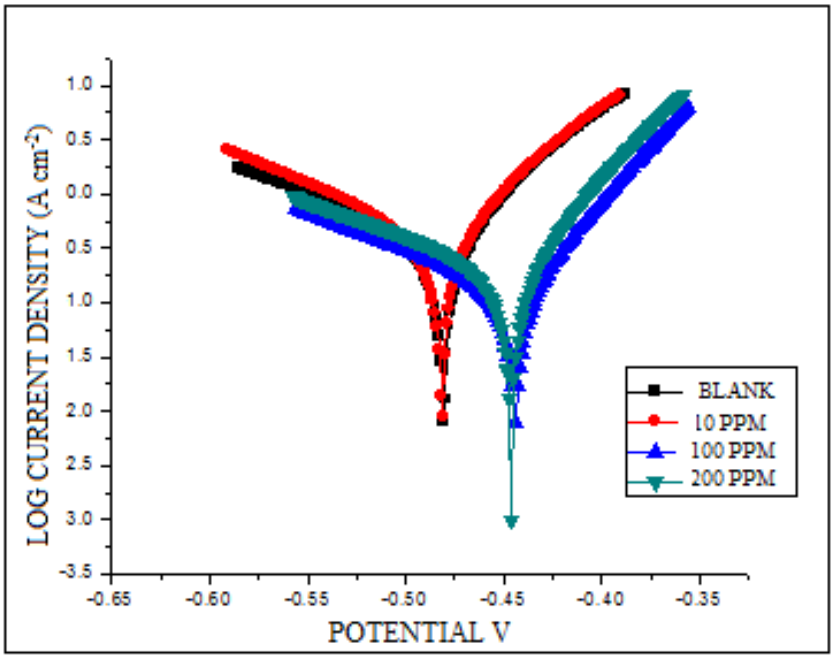


Figure 5.23 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine DPBTZ

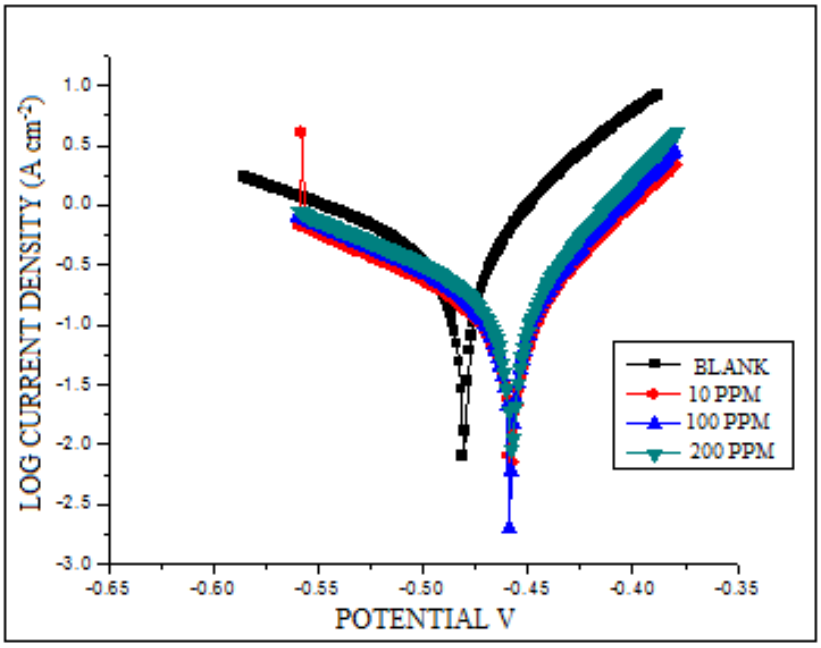


Figure 5.24 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzothiazepine EPBTZ

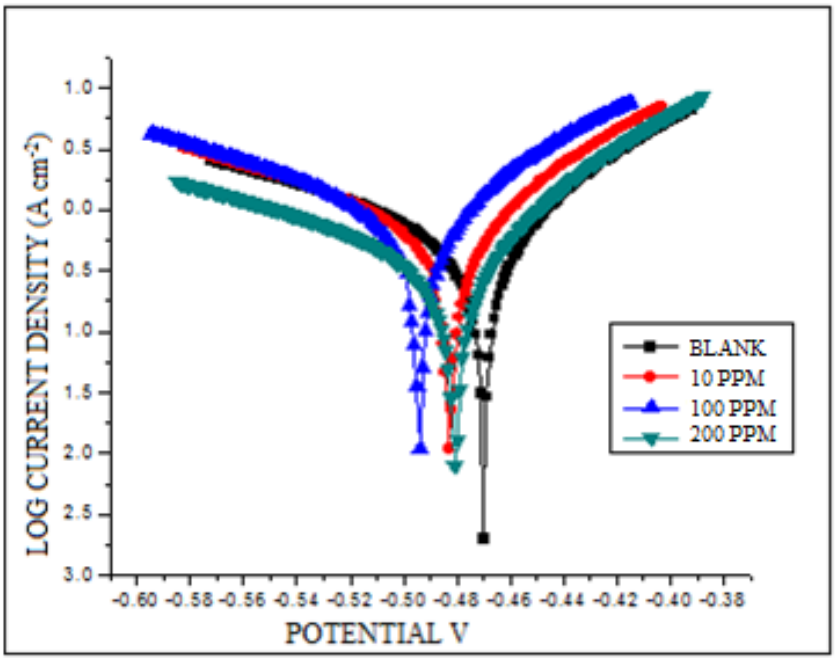


Figure 5.25 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine TMBOZ

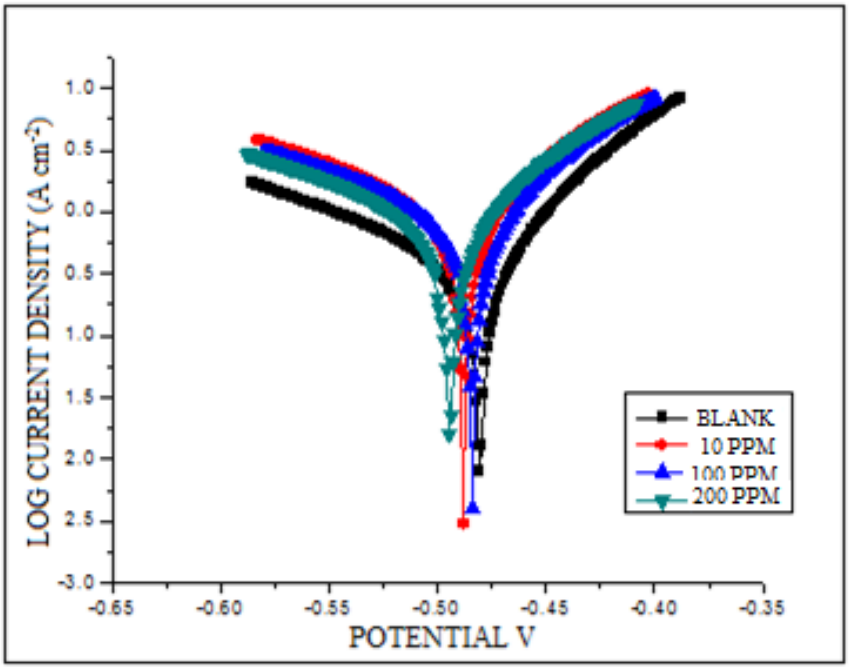


Figure 5.26 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine MBOZ

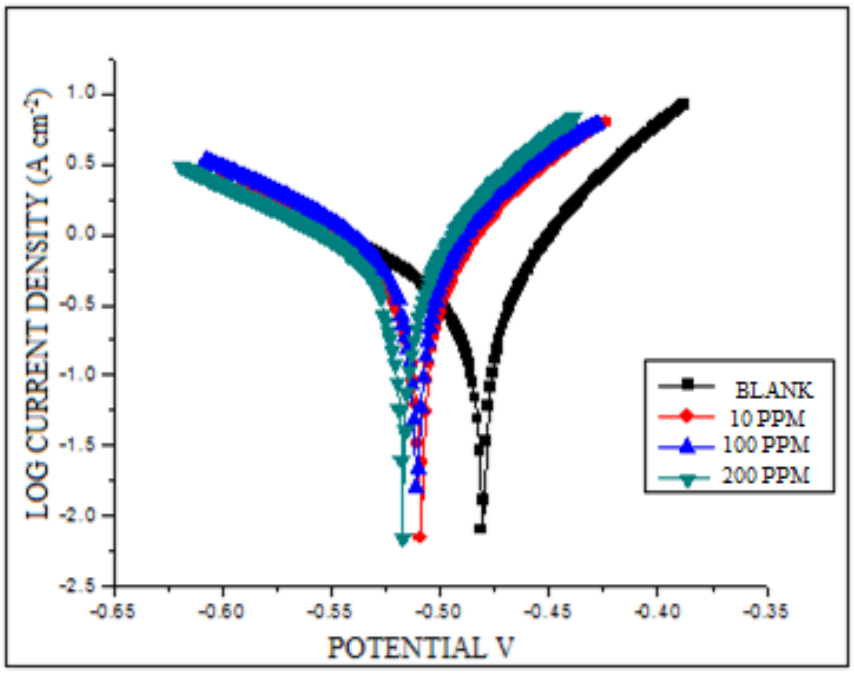


Figure 5.27 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine DPBOZ

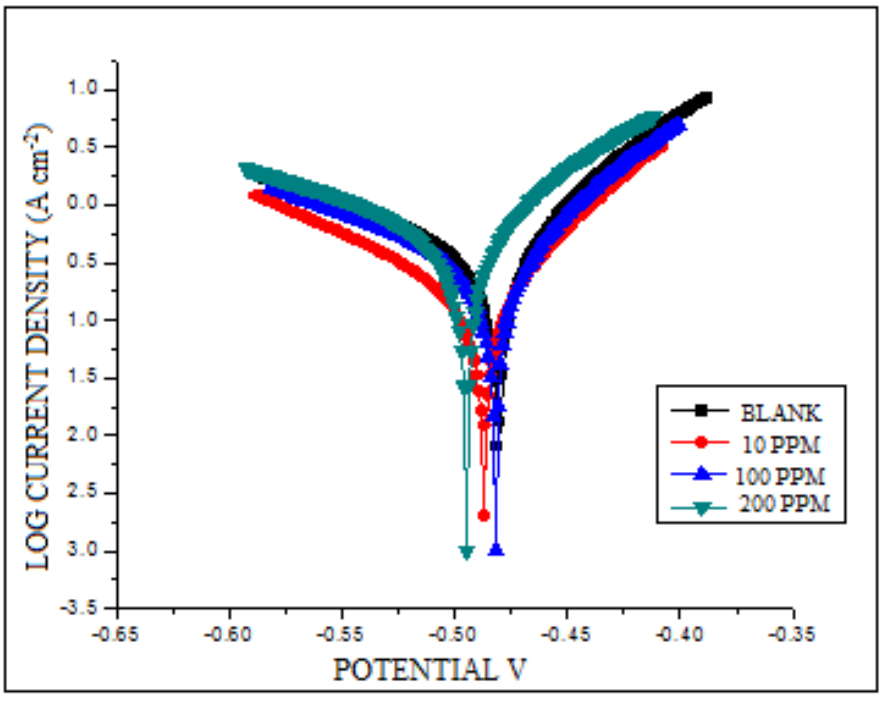


Figure 5.28 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzoxazepine EPBOZ

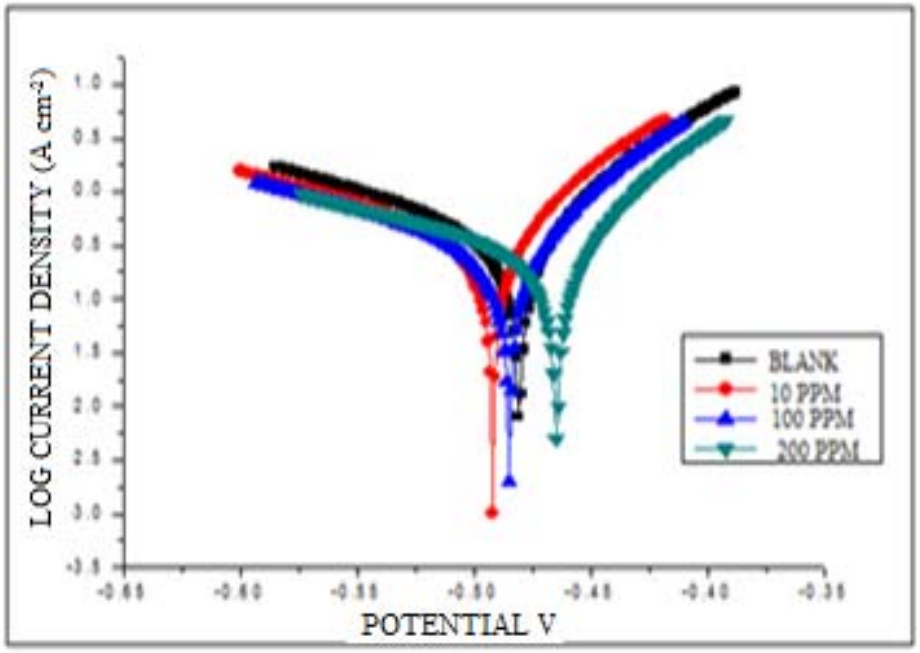


Figure 5.29 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine TMBD

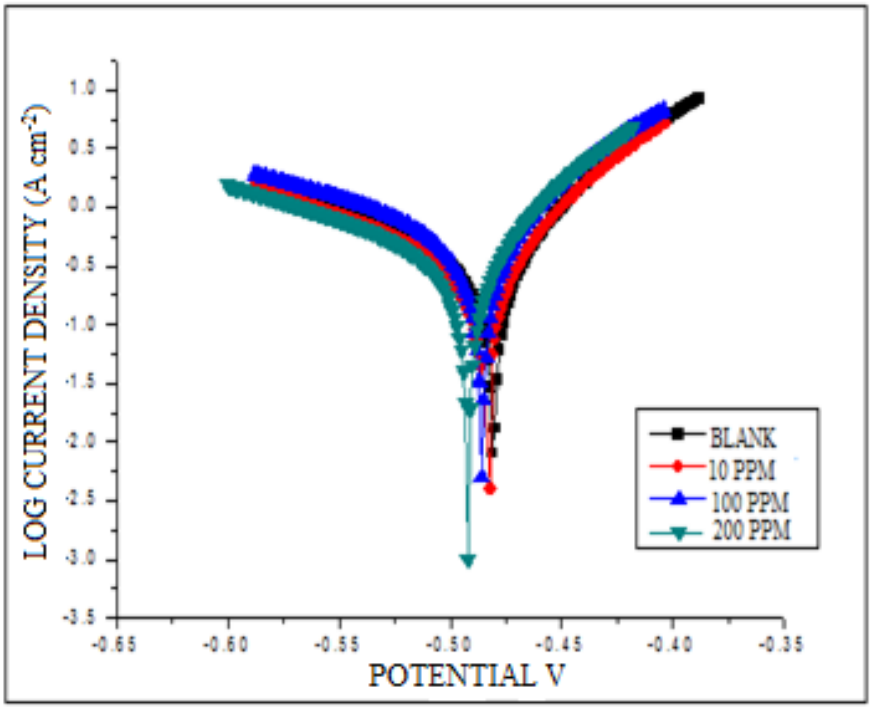


Figure 5.30 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine MBD

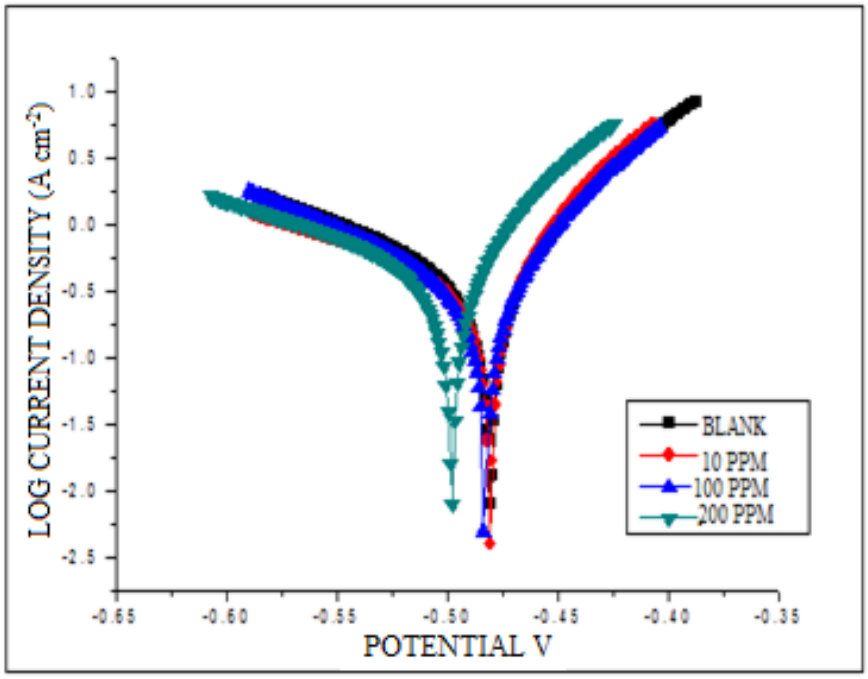


Figure 5.31 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine DPBD

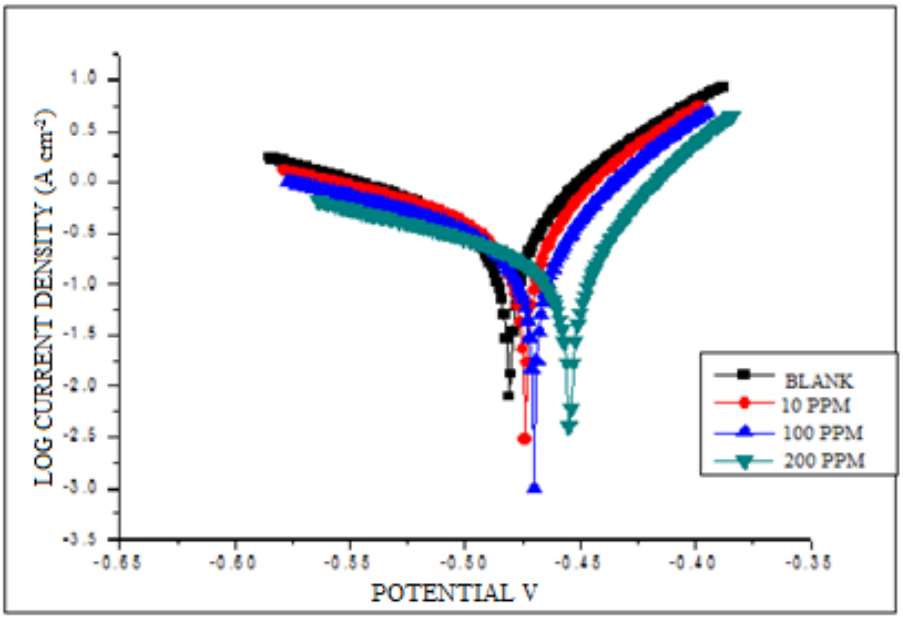
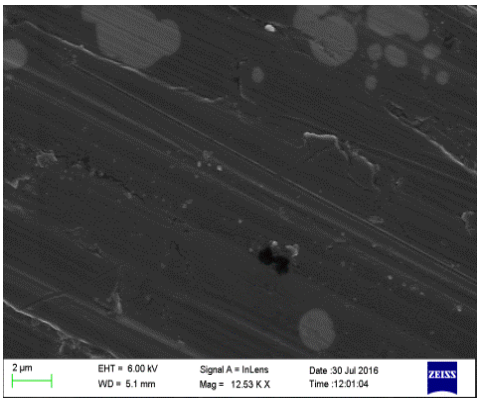
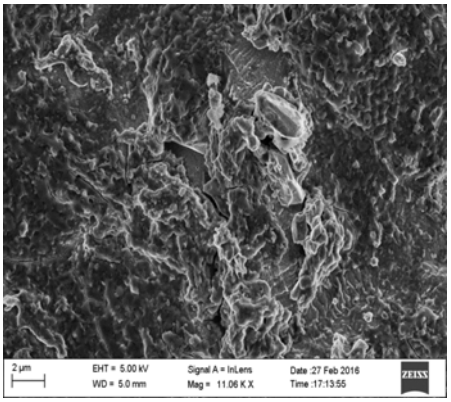


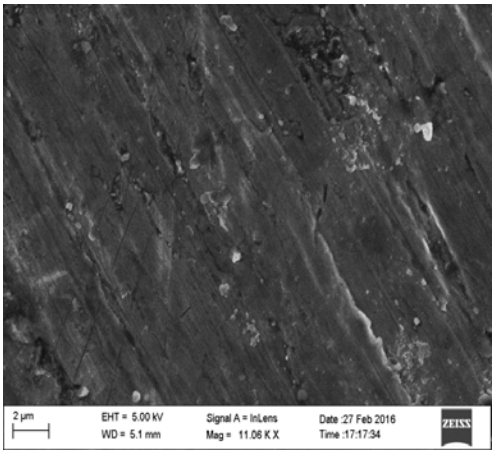
Figure 5.32 Polarization curves for mild steel in 1M H_2SO_4 for selected concentrations of benzodiazepine EPBD



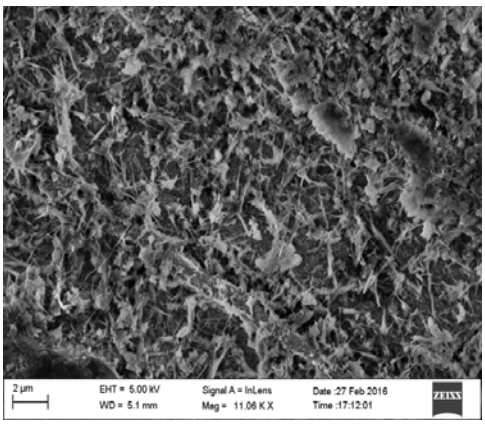
(a)



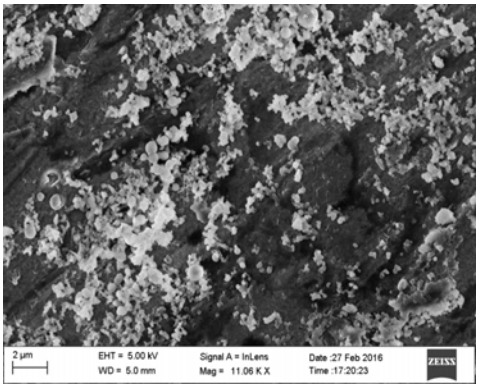
(b)



(c)

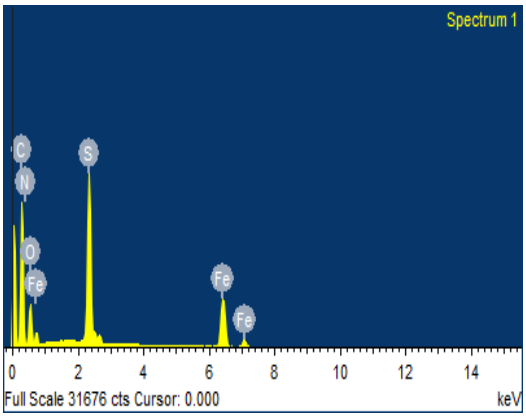


(d)

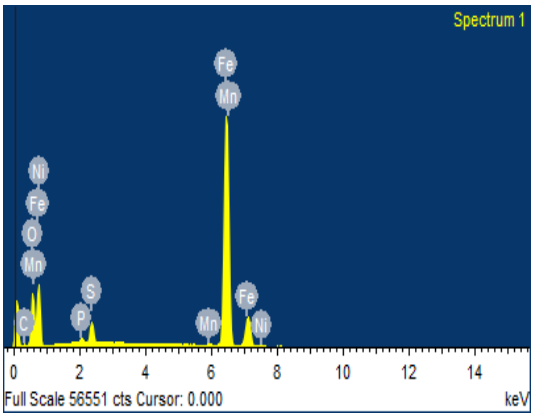


(e)

Figure 5.33 Scanning electron micrograph of (a) Polished mild steel specimen (b) After immersion in 1M H_2SO_4 (c) After immersion in 1M H_2SO_4 containing DPBTZ (d) After immersion in 1M H_2SO_4 containing DPBOZ (e) After immersion in 1M H_2SO_4 containing DPBD



(a)



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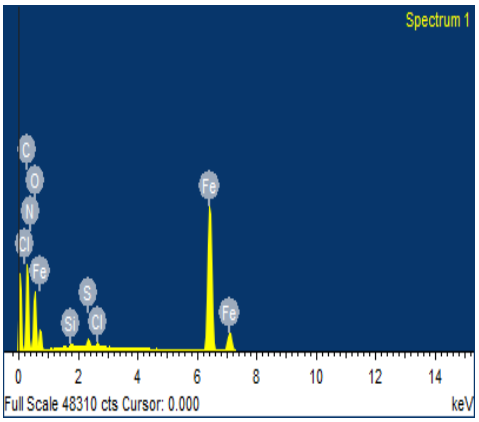

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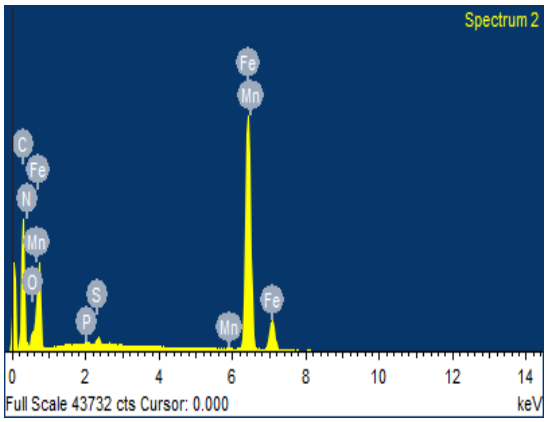

(d)

Figure 5.34 EDX spectra of mild steel immersed in (a) 1M H_2SO_4 (b) 1M H_2SO_4 containing 200 ppm DPBTZ (c) 1M H_2SO_4 containing 200 ppm DPBOZ (d) 1M H_2SO_4 containing 200 ppm DPBD