

Full Length Research Paper

Organotin dithiobiurets as corrosion inhibitors for mild steel-dimethyl sulfoxide containing HCl

R. B. Rastogi^{1*}, M. M. Singh¹, K. Singh¹ and M. Yadav²

¹Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi-221005, India.

²Department of Applied Chemistry, Indian School of Mines University Dhanbad, India.

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Corrosion inhibition studies of mild steel in dimethyl sulfoxide containing HCl have been performed at 25°C using dithiobiurets and their triphenyltin- and dibutyltin complexes as inhibitors. The inhibition efficiency (IE) of these compounds was evaluated by electrochemical polarization technique. Among the ligands, best performance was exhibited by ethoxyphenyl derivative. The IE values of the ligands enhanced appreciably on complexation. Triphenyltin complexes behaved as better corrosion inhibitors than their dibutyltin analogues. Surface studies of samples inhibited by ethoxyphenyl dithiobiuret and its organotin complexes have been made by SEM.

Key words: Mild steel, DMSO-HCl, organotin dithiobiurets.

INTRODUCTION

Mild steel is used as a structural material for reaction vessels, pipes, tank etc. which are known to corrode invariably in contact with various solvents. From the view point of nation's economy and financial implications of corrosion hazard, it is necessary to adopt appropriate means and ways to reduce the losses due to corrosion. In acidic/alkaline aqueous environments, its corrosion and prevention are well studied, however in non-aqueous solvents limited reports are available (Ekpe et al., 1995; Quraisi and Ansari, 2003; Quraisi et al., 2006; Rafiquee et al., 2007).

In particular, corrosion and inhibition of mild steel in mixed solvents containing dimethyl sulfoxide (DMSO) as one of the constituents finds rare mentioning in the literature (Posadas et al., 1970; Posadas et al., 1971: 1025; Posadas et al., 1971: 1041; Rastogi et al., 2005; Rastogi et al., 2006).

Organotins are extensively used in agriculture as efficient insecticides, bactericides, fungicides and sometimes as wood preservatives (Van der Kerk and Luitgen, 1954; Crowe 1987). Pharmacological applications of some organotins have widely been recognized

(Arakava et al., 1989; Saxena et al., 1982). Besides this, some reports are available on their usage as anticorrosive agents, (Singh and Singh, 1995; Singh and Singh, 1997; Mourad et al., 1990; Mourad et al. 1989) too. The organic compounds containing nitrogen and sulfur particularly dithiobiurets have been used as corrosion inhibitors (Quraisi et al., 2000; Quraisi et al., 1999; Rastogi et al., 2005). Since metal complexes (Singh et al., 1994; Singh et al., 1996; Singh et al., 1999; Rastogi et al., 2003; Rastogi et al., 2004) in general, have been found to possess very high corrosion inhibition efficiency, it seems plausible that the complexes of an organotin moiety and dithiobiurets may lead to higher inhibition efficiency. The present communication therefore, envisages the use of organotin dithiobiurets to reduce the corrosion rate of mild steel in dimethyl sulfoxide containing HCl.

EXPERIMENTAL

The kinetics of corrosion inhibition of mild steel in dimethyl sulfoxide medium with 0.02 M hydrochloric acid was studied using tetraethylammonium chloride as supporting electrolyte in the absence and presence of various concentrations of inhibitors at 25°C by potentiostatic polarization technique. The results obtained from these experiments have been used to explain the mechanism of corrosion inhibition.

*Corresponding author. E-mail: tofefash@yahoo.ca. Tel: 2348023063409.

Table 1. Percentage composition of working electrode specimens for electrochemical experiments.

C	Mn	Si	P	S	N	Cu	Cr	Fe
0.12	0.11	0.02	0.02	0.02	0.02	0.01	0.01	Remainder

The working electrode specimens for electrochemical experiments were prepared from mild steel sheets having the following percentage composition (Table 1).

The specimens were mechanically polished successively with 1/0, 2/0, 3/0 and 4/0 grades of emery papers. After this, the surface was thoroughly washed with soap, running tap water, distilled water and was finally degreased with acetone. The samples were dried and stored in vacuum desiccator before immersing in the test solution. The solvent DMSO was first treated with alumina and then was distilled three times under reduced pressure according to the reported method of Olabe and Arvia (1969). The water content was <1% and no traces of organic impurities were detected. The solutions have been prepared by dissolving corresponding volumes of standard hydrochloric acid in DMSO using 0.1 M tetraethylammonium chloride as supporting electrolyte.

The polarization experiments were carried out in a three necked double walled pyrex glass assembly. The cell was air-tight, containing an inlet with variable depth for nitrogen gas and an outlet with a calcium chloride tube attached to it. For applying different potentials across the reference and working electrodes, the Wenking model POS 73 potentiostat was used and the steady state current values were recorded from the ammeter on the panel of the potentiostat. A rectangular working electrode with an exposed area of 2 cm² (both sides included) was inserted through a copper rod and fixed with the help of a screw. The rest of the surface of the electrode adjacent to the exposed area was coated with extra pure paraffin wax. A platinized platinum foil of size 1×1 cm² sealed in a glass tube was used as the counter electrode. The contact was made through a platinum wire and mercury contained in the glass tube. The copper rod containing the working electrode as well as the glass tube of counter electrode was kept in a fixed position. The potential of the working electrode was measured against a saturated calomel electrode. A Luggin capillary containing KNO₃ salt bridge was used to connect the reference electrode with the cell. It was kept very close to the electrode surface to minimize IR drop. The distance between the tip of the Luggin capillary and the working electrode was kept constant in all the cases to ensure the reproducibility of the data.

Anodic and cathodic polarization experiments were performed in DMSO solutions containing various concentrations of inhibitors. The corrosion current density (i_{corr}) was determined using the Tafel extrapolation method (Evans, 1968). The corrosion rate was evaluated by using the equation,

$$0.1288 i_{corr} (E/D) \quad (1)$$

where E stands for electrochemical equivalent and D for density in gcm⁻³. For the determination of inhibition efficiencies (IEs), following equation was used;

$$\% IE = \frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \times 100 \quad (2)$$

where i_{corr}° = corrosion current density ($\mu A cm^{-2}$) in the absence of inhibitor and i_{corr} = corrosion current density ($\mu A cm^{-2}$) in the presence of inhibitors.

The surface of the specimens after polarization experiments in DMSO-HCl solutions were studied by Scanning Electron microscope JEOL-JSM. The mild steel samples were mounted on the specimen stub and inserted in the evacuated chamber of the instrument at National Electron Microscope Laboratory, Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University. Substituted dithiobiurets were prepared by the reported method (Rastogi et al., 2005). Organotin complexes were prepared by mixing methanolic solutions of organotin chloride and corresponding ligand in appropriate ratio with continuous stirring. The reaction mixture was then refluxed for two hours and the excess of solvent was distilled under reduced pressure. The residue was washed with benzene and extracted into chloroform and filtered. The crude product obtained after evaporation of chloroform was recrystallized. The compound was dried in vacuo.

RESULTS AND DISCUSSION

The percentage inhibition efficiency (IE) of 20,40,60,80 and 100 ppm of the ligands, 1-phenyl-2,4-dithiobiuret (PDTBH), 1-(3-acetylphenyl) 2,4-dithiobiuret (AcPDTBH) and 1-(4-ethoxyphenyl)-2,4-dithiobiuret (EtOPDTBH), their triphenyltin- and dibutyltin complexes have been evaluated at 25 °C and the data are recorded in Table 2. The percentage IE values exhibited by these inhibitors are appreciably high probably due to strong adsorption of the inhibitor molecules on the metal surface thereby preventing corrosion of mild steel. The parent compound PDTBH is expected to get adsorbed on the metal surface through the lone pairs of electrons on sulfur atoms which are readily available for adsorption as well as delocalized π electrons on the phenyl ring. The IE values of its derivatives are found to lie in the following order;



It is interesting to note that the substitution of $-OC_2H_5$ and $-COCH_3$ to the same parent compound resulted in entirely opposite impact on IE values. The substitution of both these groups was expected to improve the inhibition efficiency of the parent compound by enlarging the surface area and increasing one more active centre in the form of oxygen atom. The observed data indicate that there had been no increase in the projected surface area of the molecule and oxygen could not act as an active centre owing to the m- directing nature of acetyl group in AcPDTBH. However, in case of EtOPDTBH, $-OC_2H_5$ occupies p- position and therefore, there is some increase in projected surface area. Further, explanation of the observed data can be offered in terms of +I and -I effect of the two substituents. The ethoxy group at

Table 2. Percentage inhibition efficiency %IE values calculated by polarization technique in presence of dithiobiurets and their triphenyltin(IV) and dibutyltin(IV) complexes.

Concentration (ppm)	Ligand (PDTBH)	(Bu ₂) Sn(PDTB) ₂	(Ph ₃) Sn PDTB
20	50.62	58.87	69.46
40	57.23	66.69	75.32
60	65.32	73.28	79.08
80	70.03	76.46	81.11
100	75.42	80.03	84.30

Concentration(ppm)	Ligand (AcPDTBH)	(Bu ₂) Sn(AcPDTB) ₂	(Ph ₃)Sn AcPDTB
20	46.13	52.84	65.32
40	51.65	57.54	71.81
60	58.39	64.59	73.70
80	64.26	68.37	76.55
100	68.32	74.88	79.80

Concentration(ppm)	Ligand(EtOPDTBH)	(Bu ₂)Sn(EtOPDTB) ₂	(Ph ₃)SnEtOPDTB
20	58.72	68.48	74.13
40	67.60	75.09	82.86
60	72.32	78.69	85.43
80	76.11	82.47	87.08
100	82.32	86.92	91.85

p-position acts as an electron donating group and therefore the electron density of delocalized π electrons on phenyl ring increases. This results in stronger bonding with the metal surface through the participation of π electrons. In case of AcPDTBH, -COCH₃ at m-position acts as an electron withdrawing group and hence the efficiency decreases. It is noticeable that there is tremendous increase in IE values of the complexes as compared to the respective ligands. Further, the order of IE of these complexes remains the same corresponding to the respective ligands.

Ph₃Sn (EtOPDTB) > Ph₃Sn (PDTB) > Ph₃Sn (AcPDTB)
 Bu₂Sn (EtOPDTB)₂ > Bu₂Sn(PDTB)₂ > Bu₂Sn(AcPDTB)₂
 Ph₃SnPDTB > Bu₂Sn (PDTB)₂ > PDTBH

Among the complexes, triphenyltin complexes exhibit comparatively higher IE than their dibutyltin analogues. The difference in their behavior may be discussed in light of active centres for adsorption, structural difference, if any, and their projected surface area. The structure for triphenyltin dithiobiurets is tentatively proposed as trigonal bipyramidal where the ligand being bulky occupies two of the equatorial positions and the rest of the sites occupied by phenyl groups. Since DMSO is a strong coordinating solvent, dissolution of complex has resulted in transition of stereochemistry from trigonal bipyramidal to octahedral as shown in Figure 1. The structure for dibutyltin dithiobiurets is proposed to be octahedral.

Thus, as far as, their geometry is concerned both the

complexes possess similar structure in DMSO. However, a critical examination of the structure of these complexes reveals that the probable sites of adsorption are different in triphenyltin and dibutyltin complexes. Apparently three phenyl rings attached to tin atom and nitrogen, sulfur and phenyl ring of the ligand dithiobiuret could act as the active sites for adsorption in case of triphenyltin complexes. On the other hand, in the case of dibutyltin complexes, sulfur, nitrogen and phenyl ring of both dithiobiuret groups may be considered to be the active sites for adsorption. It is further apparent from the structures that all the active sites in both categories of the complexes cannot participate in the adsorption process simultaneously. Therefore, their IE values cannot be correlated with the number of active sites present on them.

Dibutyltin complexes appear to be quite symmetrical in structure. But in any case, the adsorption of these molecules would occur strictly from one of the ligand groups only at a time. Thus, in spite of larger molecular size, the increase in IE does not occur to the same extent as anticipated in terms of the presence of two dithiobiuret groups.

In case of triphenyltin dithiobiurets their adsorption on the metal surface may occur through the participation of one of the phenyl rings attached directly to the tin atom as well as dithiobiuret. This seems to be the actual case in the light of their unsymmetrical structures. It is very likely that in the event of adsorption through the phenyl ring attached to tin atom the molecule will tilt such that the ligand group could also participate in adsorption. This

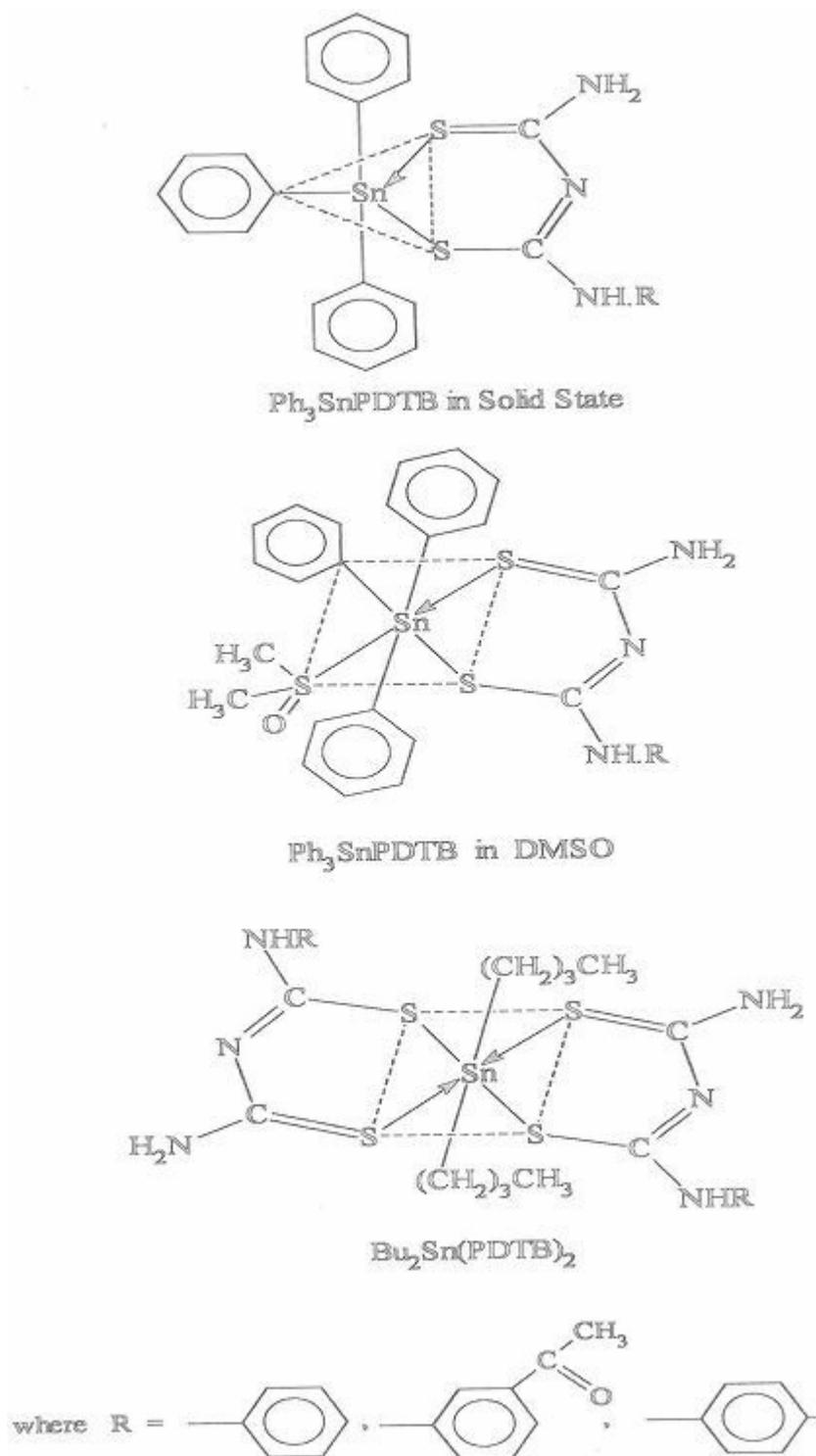


Figure 1. Structure of organotin dithiobiurets.

would result in the coverage of larger projected area than that anticipated. Therefore, triphenyltin complexes should show better IE than the corresponding dibutyltin complexes, which is the actual case.

Anodic polarization behavior of mild steel in HCl-DMSO containing 20, 40, 60, 80 and 100 ppm of PDTBH is shown in Figure 2. It is apparent from the figure that the nature of the curve for the blank solution is not affected

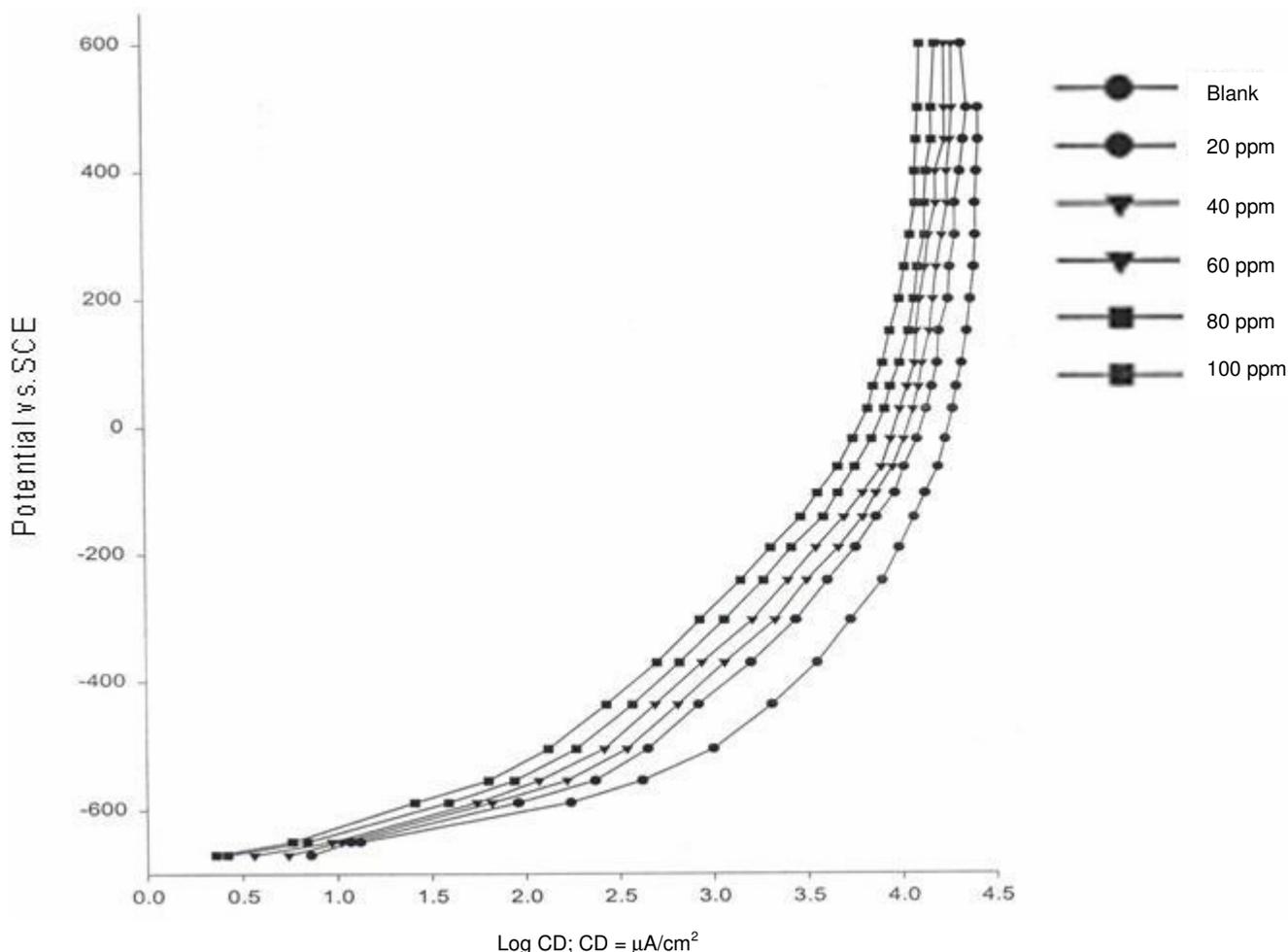


Figure 2. Anodic polarisation behaviour in absence and presence of concentration of PDTBH.

by the addition of the inhibitor and subsequent increase in its concentration. This indicates that there is no change in the mechanism of corrosion on the addition of the inhibitors (Kumar et al., 1998). However, in presence of 20 ppm of inhibitor the curves shifted towards lower current density region at each potential with respect to the curve without inhibitor. A further increase in concentration of the inhibitor up to 100 ppm resulted in a further decrease in the current density, but the magnitude of decrease in current density is not significant. This indicates that adsorption sites are saturated on increasing concentration of the inhibitor. The anodic polarization curves for all derivatives that is, phenyl-,3-acetylphenyl and 4-ethoxyphenyl of dithiobiuret studied at fixed concentration of 100 ppm at 25°C have been illustrated in Figure 3. Maximum shift towards lower current density is observed for 1-(4-ethoxyphenyl)-2,4-dithiobiuret which shows maximum %IE whereas minimum shift is observed for 1-3-acetylphenyl -2,4-dithiobiuret which gives minimum IE.

The anodic polarization behavior of mild steel in HCl-DMSO system containing 20,40,60,80 and 100 ppm of triphenyltin complex of 1-phenyl-2, 4- dithiobiuret is shown in Figure 4. The nature of curves for the complex is similar to the curves obtained in the presence of respective ligands and in the blank solution, showing that there is no change in the mechanism of corrosion on the addition of triphenyltin complex of dithiobiuret as inhibitor. However, shift towards lower current density in case of the complex is larger than the corresponding ligand indicating that triphenyltin complex is more effective as an inhibitor than the corresponding ligand. A decrease in the corrosion current density and an increase in the inhibition efficiency were found to be maximum at the 100 ppm of inhibitor. This effect can possibly arise because of the adsorption of $(\text{Ph})_3\text{Sn}$ PDTBH leading to reduced bare surface of the metal surface where corrosion could occur. Figure 5 depicts a comparative polarization behavior of the studied triphenyltin dithiobiurets at a particular concentration of 100 ppm. It is apparent from the figure

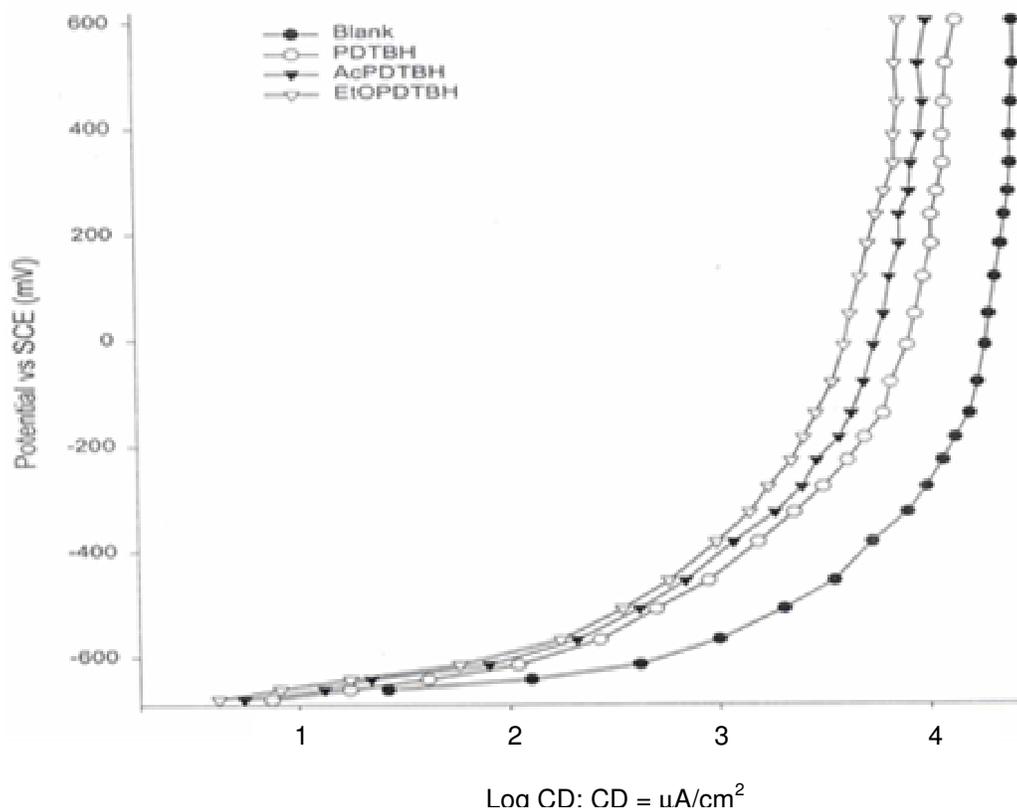


Figure 3. Anodic polarisation behaviour in absence and presence of 100 ppm of different dithiobiurets.

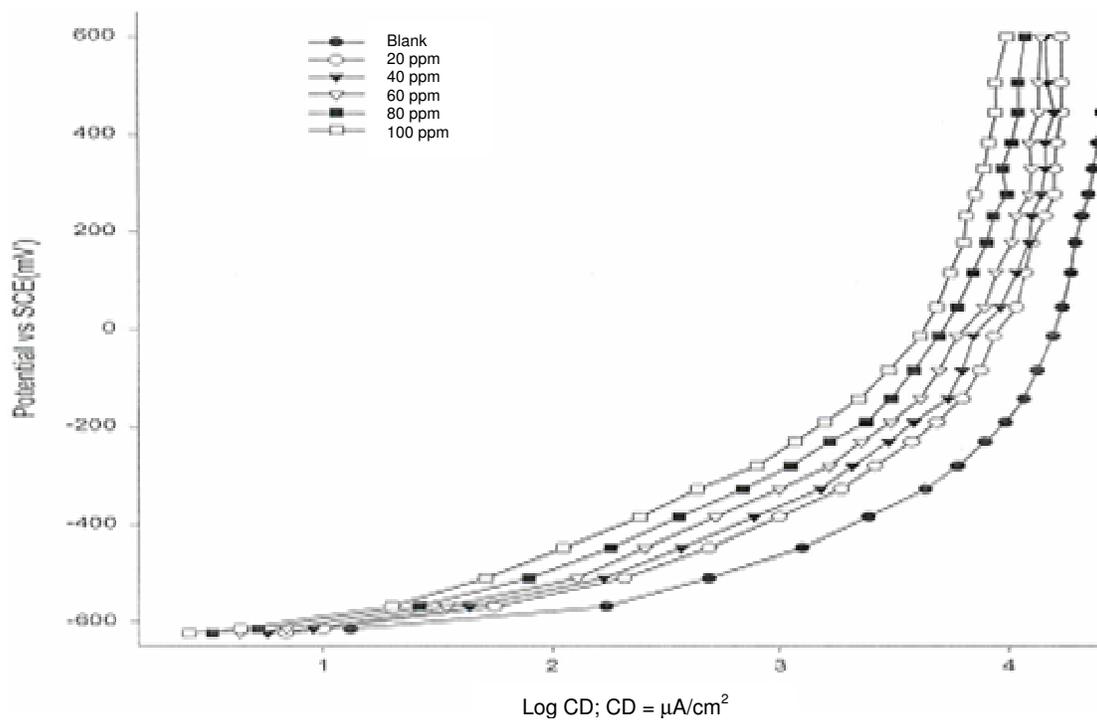


Figure 4. Anodic polarisation behaviour in absence and presence of 100 ppm of different concentration of (Ph)₃SnPDTB.

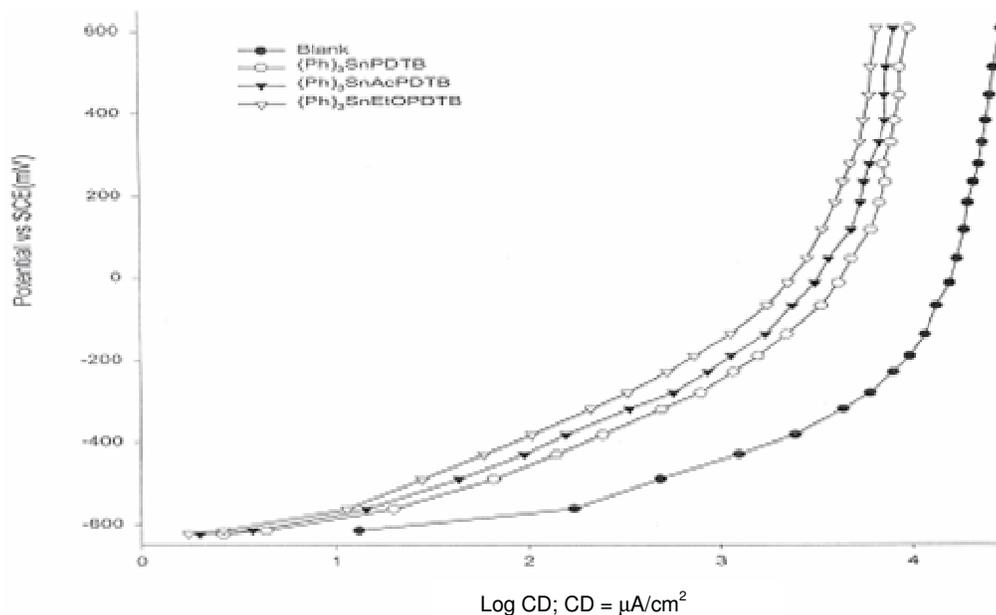


Figure 5. Anodic polarisation behaviour in absence and presence of 100 ppm of triphenyltin dithiobiurets.

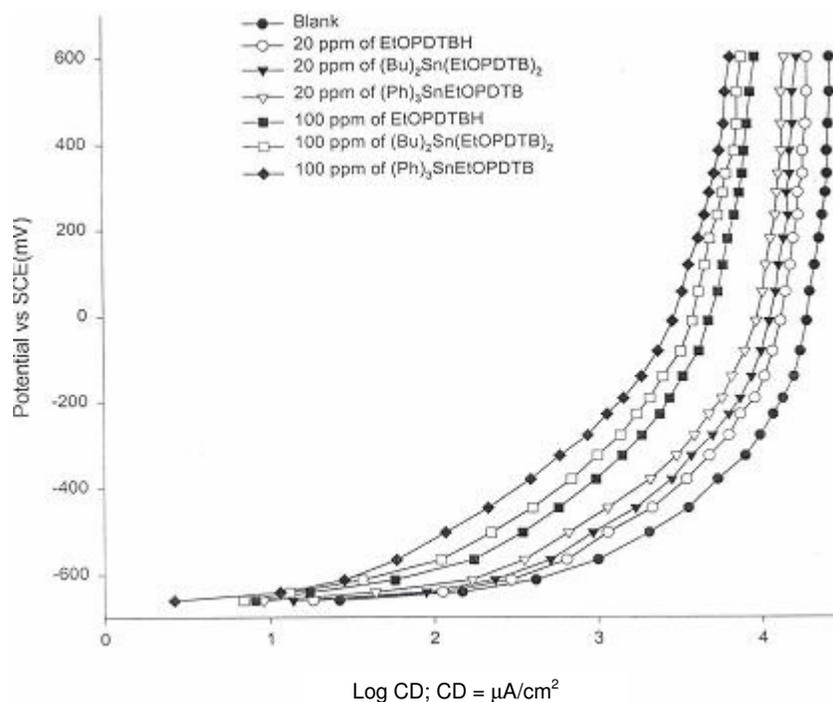


Figure 6. Anodic polarisation behaviour in absence and presence of 20 and 100 ppm of EtOPDTBH and its organotin complexes.

that the order of the shifts of the curves (and consequently the % IE of the complexes) follows the same order as that of the respective ligands.

Anodic polarization behavior of dibutyltin complexes of

dithiobiurets has been studied at the concentrations same as those of triphenyltin complexes of same ligands. Figure 6 shows the Anodic polarization behavior of mild steel in HCl-DMSO in presence and absence of 20 and

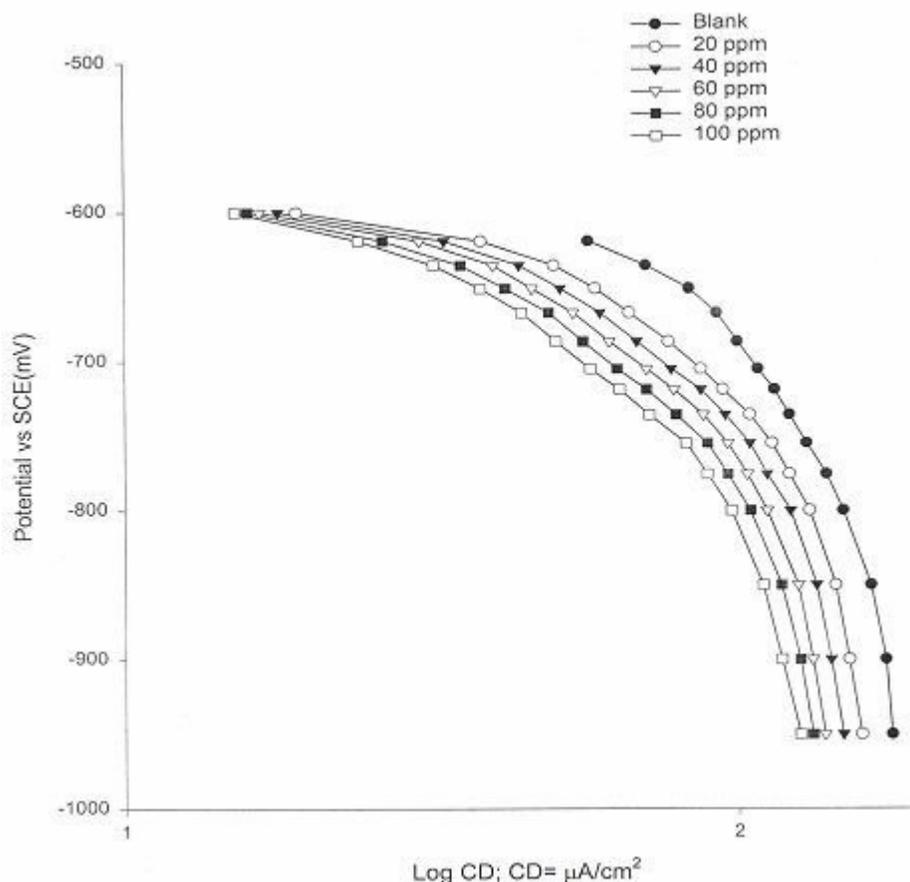


Figure 7. Cathodic polarisation behaviour in absence and presence of PDTBH.

100 ppm of 1-(4-ethoxyphenyl)-2,4-dithiobiuret and its triphenyltin and dibutyltin complexes. The nature of curves is almost the same as in the case of the ligand and its triphenyltin complex. An appreciable decrease in the current density at higher potential indicates the potential dependent nature of the process. Magnitude of such shift depends on the type of inhibitors and their concentration. The maximum decrease in the current density is found for triphenyltin complex followed by dibutyltin complex and then the corresponding 1-(4-ethoxyphenyl)-2, 4-dithiobiuret ligand. It is also noticed that the extent of shift of anodic curves in case of triphenyltin and dibutyltin complexes at 100 ppm is more as compared to the shift at 20 ppm. It shows that decrease in corrosion current density is more appreciable at higher concentrations of inhibitors.

Figure 7 illustrates the cathodic polarization curves in the presence of different concentrations of 1-phenyl-2-4-dithiobiuret at 25°C. It is noticed that the curves shift towards lower current density with respect to the blank curve. A further shift in the curves on increasing concentration, very similar to that noticed in the case of anodic polarization behavior is observed. It may be

further noted that the cathodic shift on addition of a given amount of the inhibitor is more significant than the corresponding anodic shift. The cathodic polarization curves for all derivatives of dithiobiuret at 25°C with 100 ppm of inhibitor concentration have been shown in Figure 8. It is observed that maximum shift towards lower current density is observed for 1-(4-ethoxyphenyl)-2,4-dithiobiuret which shows maximum IE and minimum shift is observed for 1-3-acetylphenyl -2,4- dithiobiuret with minimum IE. Figure 9 shows the cathodic polarization curves in presence of different concentrations of triphenyltin complex of 1-phenyl-2-4-dithiobiuret at 25°C. It is observed that nature of curves remain the same but shift in curves is more marked than that due to 1-phenyl-2-4-dithiobiuret ligand. The cathodic polarization curves for triphenyltin complexes of all derivatives of the ligand dithiobiuret at 25°C at a fixed concentration of 100 ppm are shown in Figure 10. It is observed again that the shift towards lower current density in these curves is greater as compared to the corresponding ligands. The maximum shift towards lower current density is exhibited by triphenyltin complex of 1-(4-ethoxyphenyl)-2,4-dithiobiuret which shows maximum IE. Figure 11 shows

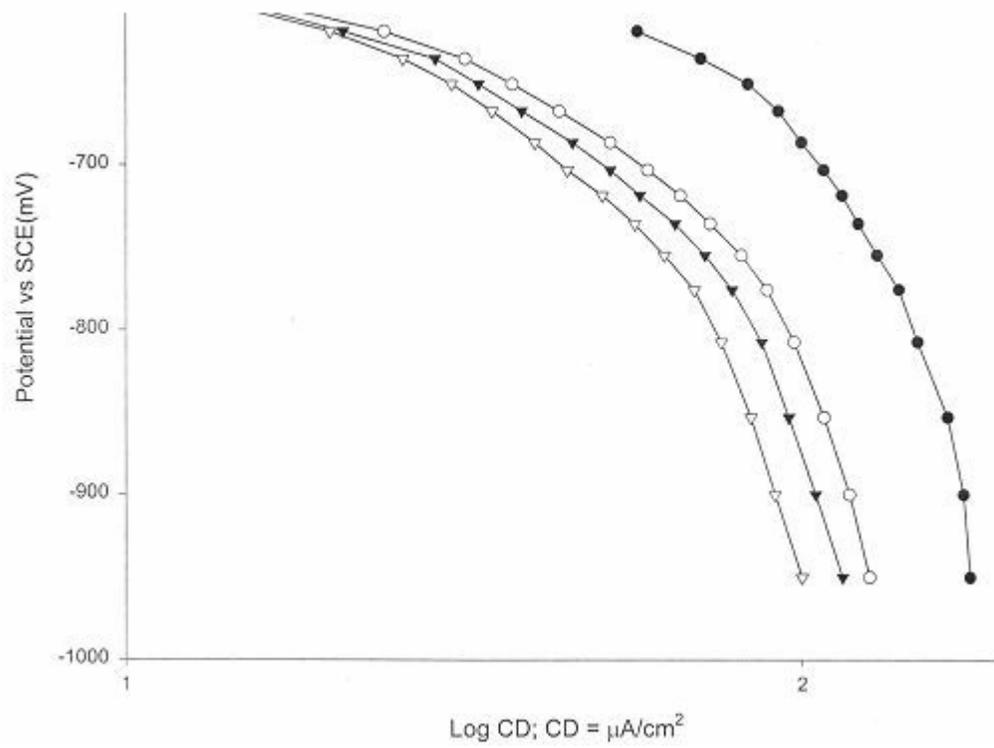


Figure 8. Cathodic polarisation behaviour in absence and presence of 100 ppm of dithiobiurets.

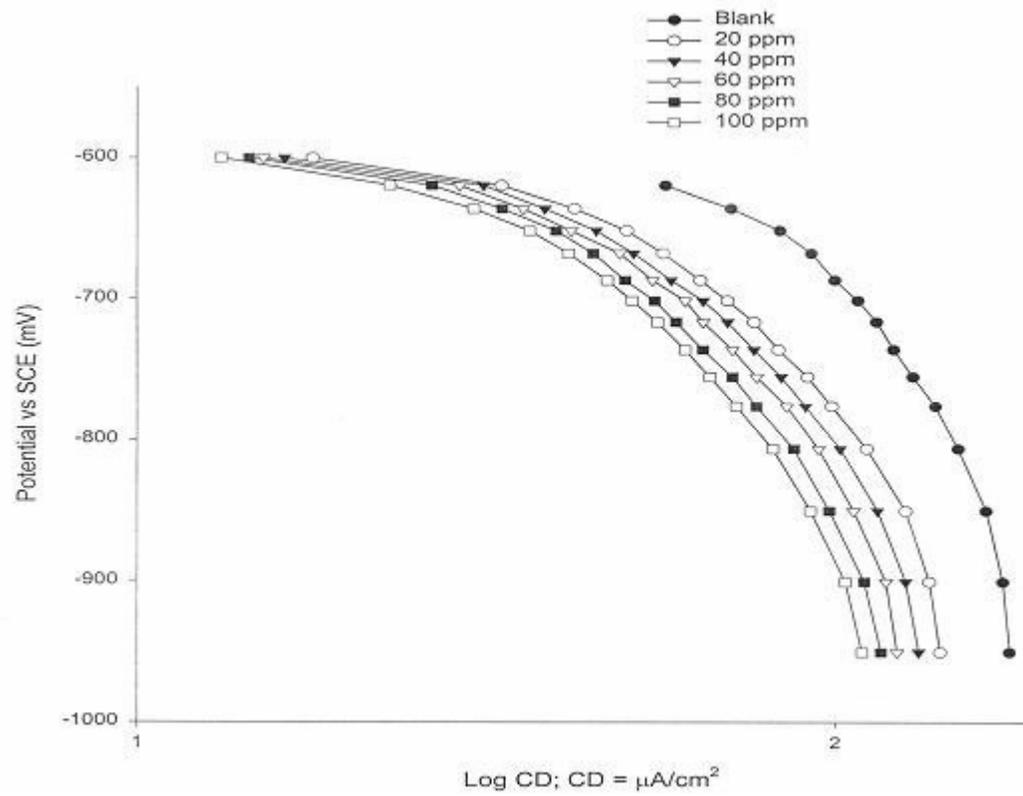


Figure 9. Cathodic polarisation behaviour in absence and presence of different concentrations of $(\text{Ph})_3\text{SnPDTB}$.

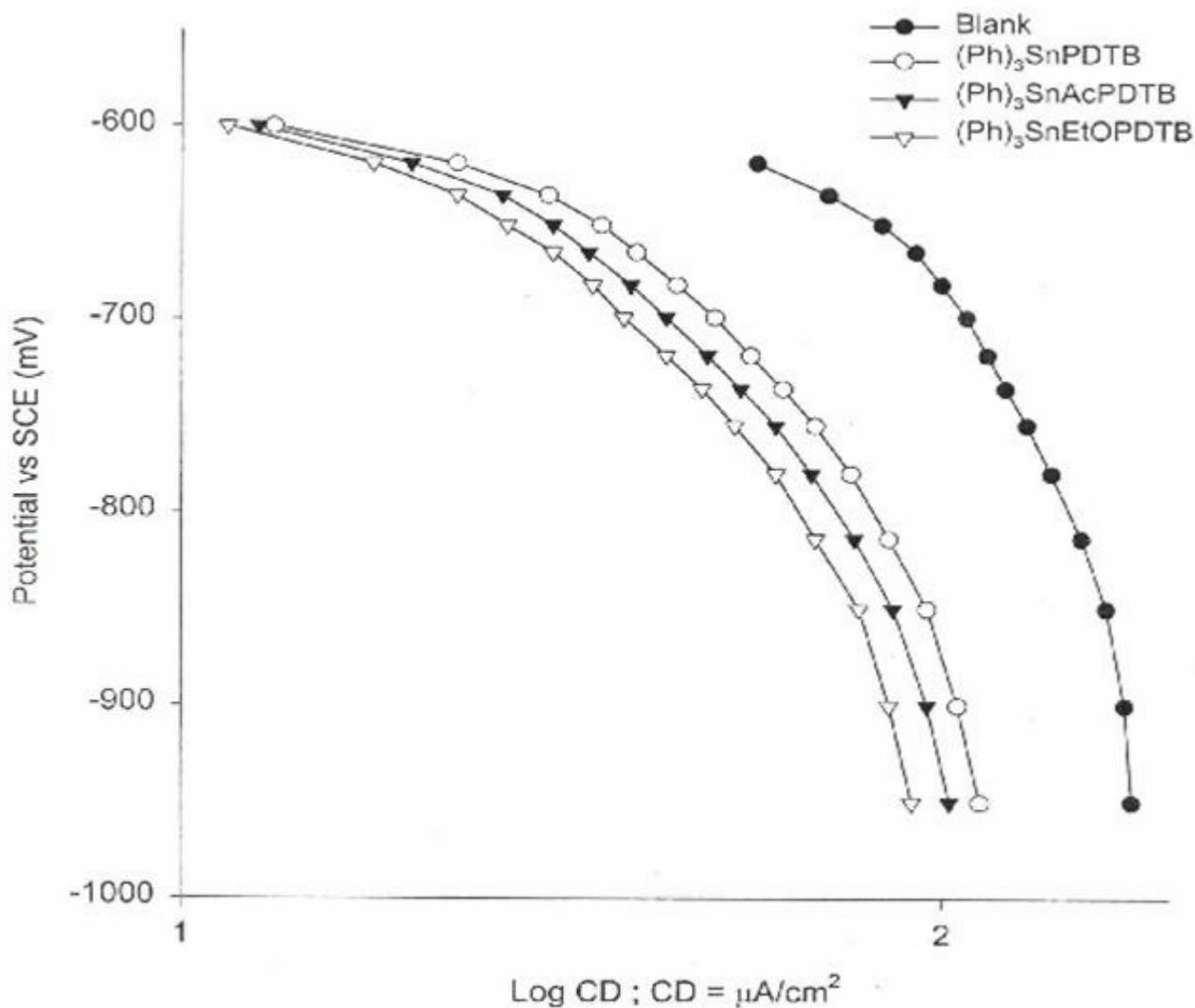


Figure 10. Cathodic polarisation behaviour in absence and presence of 100 ppm of triphenyltin dithioburets.

the comparison of the extent of shift of cathodic curves towards lower current density for 1-(4-ethoxyphenyl)-2,4-dithiobiuret and its triphenyltin and dibutyltin complexes at 20 and 100 ppm concentration respectively at 25°C. The trend in the shift of these curves is observed to be same as the shift in anodic polarization curves for the same compounds. From the shifting of curves of anodic and cathodic polarization it is observed that the shift of cathodic curves is more pronounced as compared to the anodic curves. Thus, it may be inferred that these compounds are predominantly cathodic inhibitors.

The adsorption of inhibitors is governed by the residual charges on the surface of the metal and by the nature and chemical structure of the inhibitor. Assuming that the percentage area covered by the inhibitors is directly proportional to retardation in the corrosion rate, the compound should obey either the Langmuir or those of Temkin or Frumkin Adsorption Isotherms (Gupta and

Singh, 1999). The experimental equation of Frumkin isotherm (Damaski et al., 1968; Gileadi, 1967).

$$\frac{\theta}{1-\theta} \exp(f\theta) = KC \quad (3)$$

where 'K' is equilibrium constant for the adsorption reaction and 'C' is the concentration of the inhibitor in mole litre⁻¹, is the degree of coverage and 'f' is a parameter connected with the variation of adsorption energy with coverage. Langmuir isotherm is obtained for f=0 and may be written as;

$$\log \frac{\theta}{1-\theta} = \log A + \log C - \frac{Q}{2.3RT} \quad (4)$$

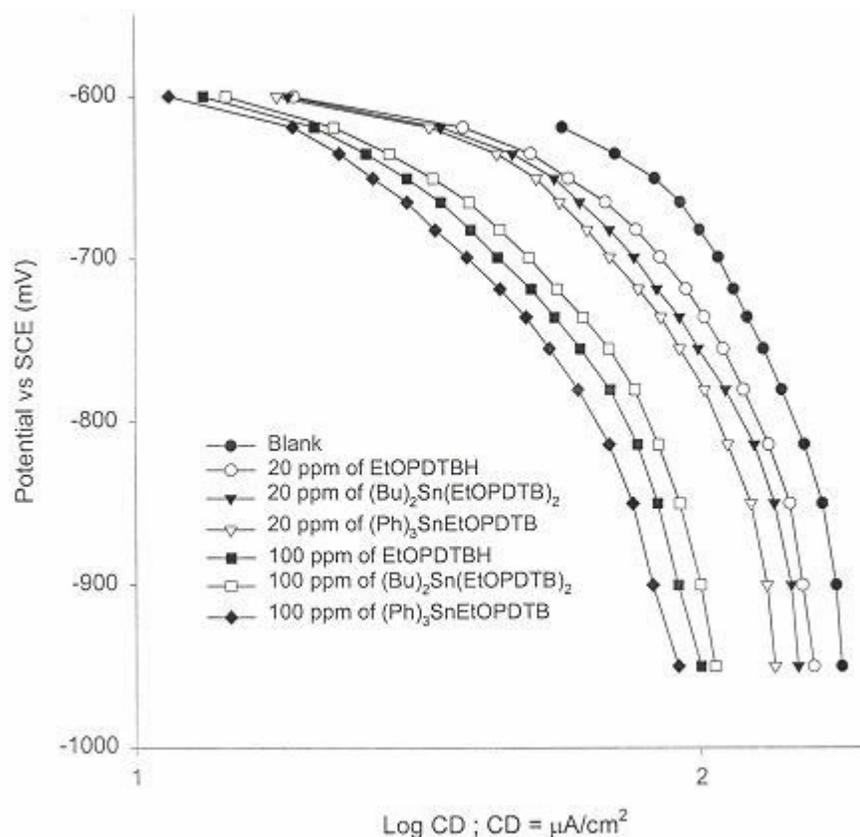


Figure 11. Cathodic polarisation behaviour in absence and presence of 20 and 100 ppm of EtOPDTBH and its organotin complexes.

where A and Q are temperature independent constant and heat of adsorption, respectively. The validity of Langmuir isotherm is confirmed from the linearity of the $\log \theta / 1 - \theta$ vs. $\log C$ plot having the slope value to be unity.

The plots of $\log \theta / 1 - \theta$ vs. $\log C$ for the investigated dithiobiurets, their triphenyltin and dibutyltin complexes at 25°C are shown respectively in Figure 12. It was observed that although these plots were linear, the gradients were never unified, contrary to what was expected for the ideal Langmuir isotherm equation. The departure in the values of the slopes of Langmuir plots from unity may be advocated to be due to mutual interaction between adsorbed molecules in close vicinity. Organic molecules and metal complexes having polar atoms or groups which are adsorbed on the metal surface may interact by mutual interaction and hence may affect the heat of adsorption. A plot of θ vs. $\log C$ for the dithiobiurets and their triphenyltin and dibutyltin complexes gave a straight line, indicating the validity of Temkin's isotherm Figure 13. Thus the adsorption of these inhibitors obeys Temkin's adsorption isotherm.

Figure 14 shows the scanning electron microphotographs of mild steel in HCl-DMSO in the presence of

100 ppm of 1-(4-ethoxyphenyl)-2, 4- dithiobiuret, its dibutyltin and triphenyltin complexes at $\times 75$ magnification. On comparing these microphotographs, it appears that maximum smoothing of the surface of test material has been observed in presence of the triphenyltin complex followed by the dibutyltin complex and then the dithiobiuret. This observation is in conformity with the observed inhibition efficiency values as discussed earlier.

Conclusions

1. All the compounds were found to be efficient corrosion inhibitors.
2. Among dithiobiurets, ethoxyphenyl derivative exhibited maximum inhibition efficiency followed by phenyl and then acetylphenyl derivatives.
3. The IEs of organotin complexes were observed to be appreciably higher than the respective ligands.
4. Triphenyltin complexes proved to be better inhibitors than their dibutyltin analogues.
5. Organotin complexes behaved predominantly as cathodic inhibitors.

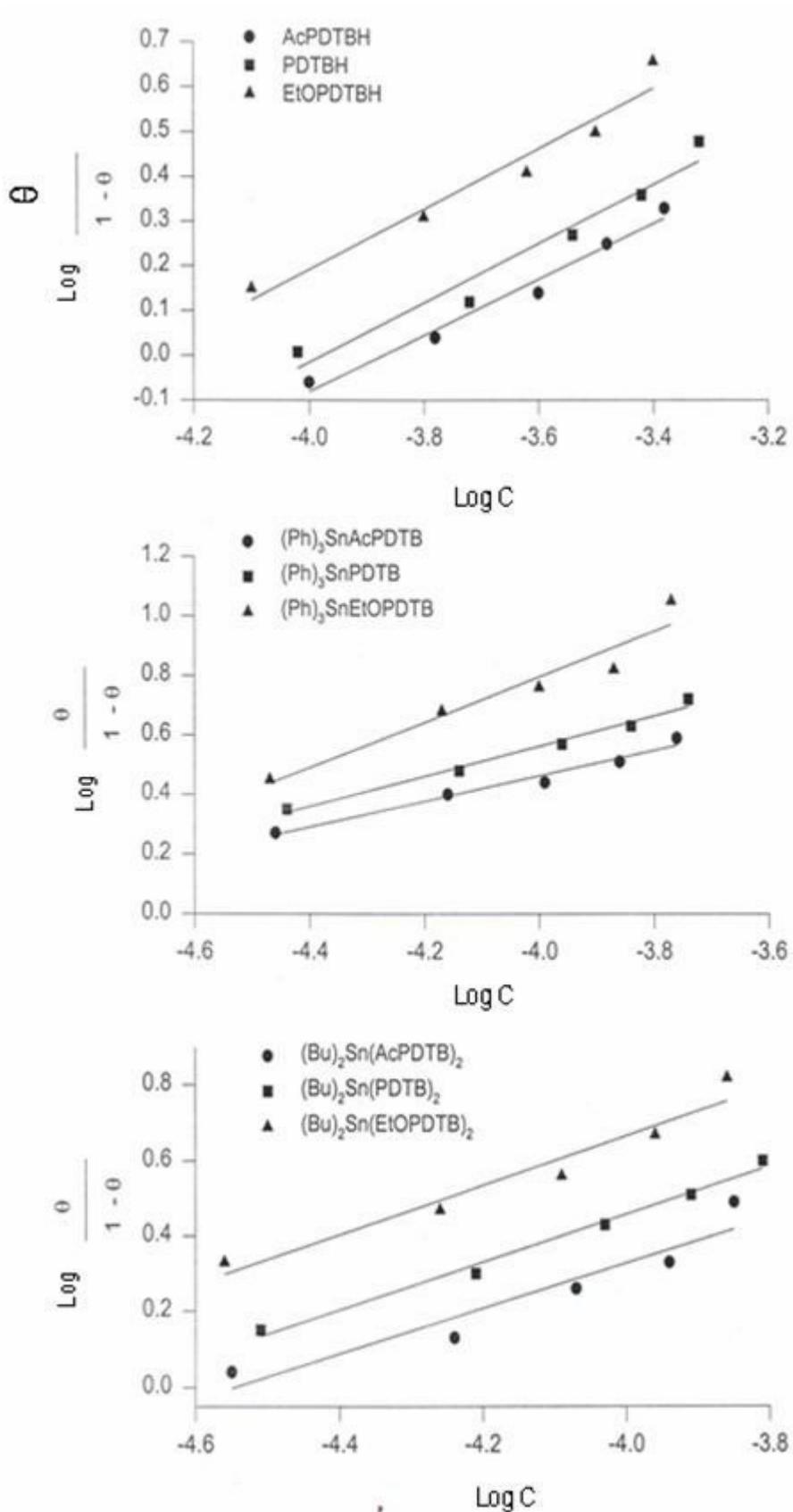


Figure 12. Langmuir plots for dithiobiurets and organotin complexes.

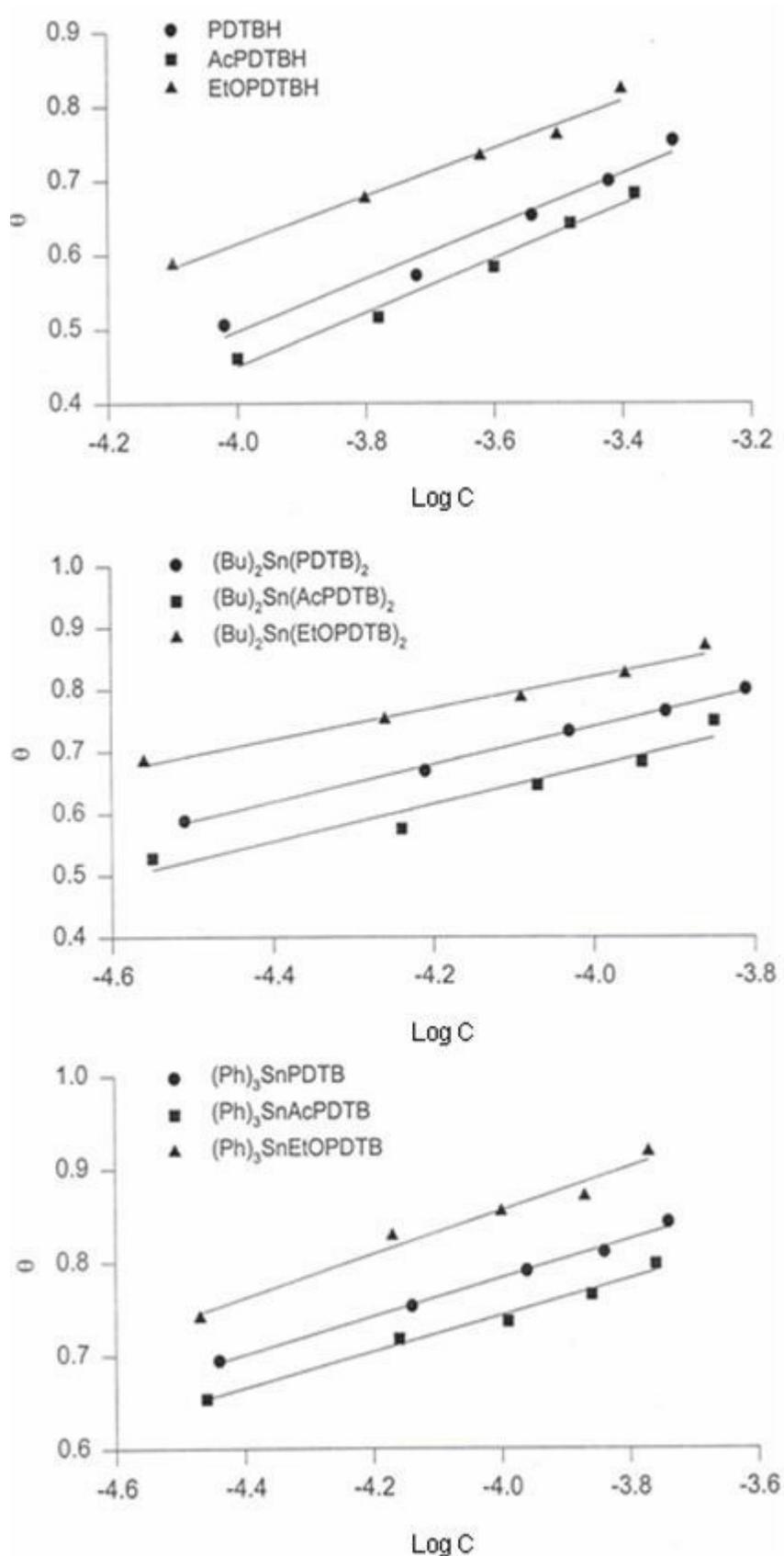


Figure 13. Temkin plots for dithiobiurets and organotin complexes.

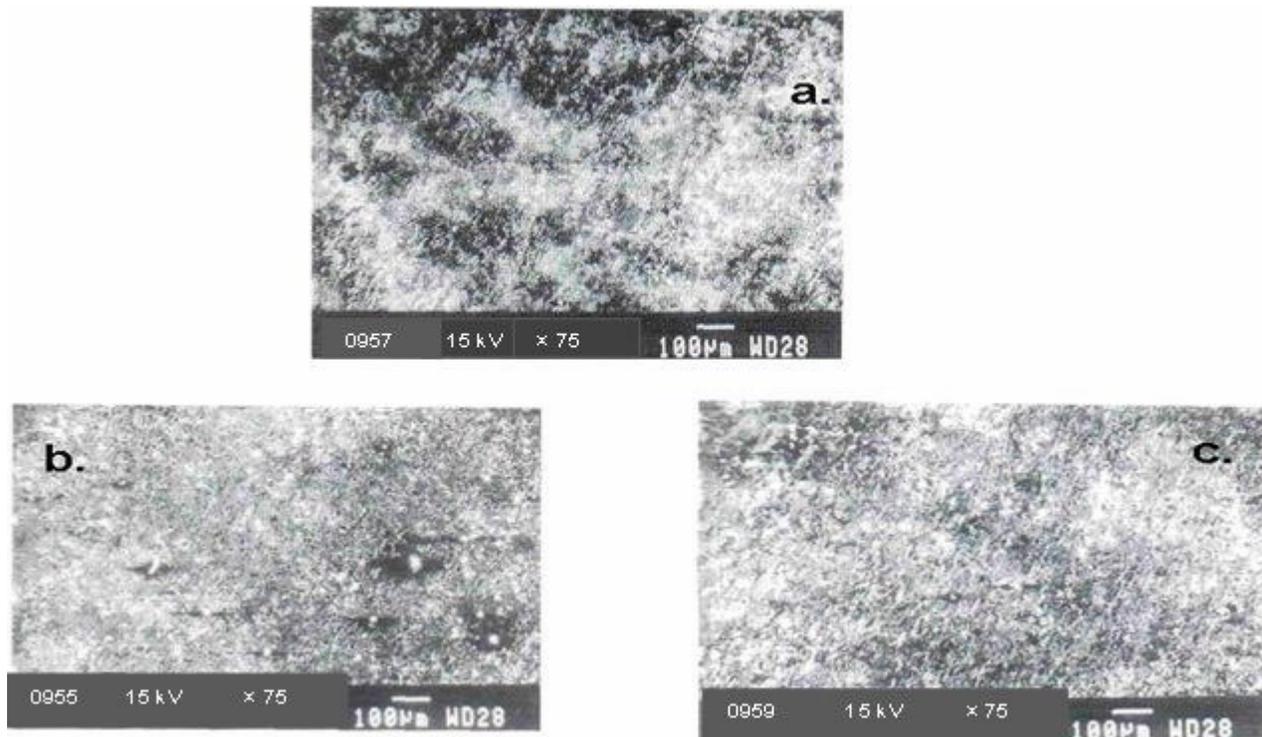


Figure 14. SEM photographs of milds steel in presence of (a) EtOPDTBH, (b) $\text{BU}_2\text{Sn}(\text{EtOPDTB})_2$ and (c) $\text{Ph}_3\text{Sn}(\text{EtOPDTB})$.

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