Synthesis and Potency Study of Some Dibutyltin(IV) Dinitrobenzoate Compounds as Corrosion Inhibitor for Mild Steel HRP in DMSO-HCl Solution

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Following our succes in the synthesis of some derivatives of organotin(IV) carboxylates, in this work we reported the corrosion inhibitor study of three dibutyltin(IV) compounds using ligands of 2-, 3- and 4-nitrobenzoic acid. All the three synthesized compounds were characterized by spectroscopy techniques and also based on the microanalytical and physical data. The corrosion inhibition was evaluated with potentiodynamic polarization technique using ER644 Integrated Potentiostat eDAQ type on mild steel hot rolled plate (HRP) in DMSO-HCl solution. The results indicated that the these compounds showed interesting inhibition activity with percentage of inhibition efficiency (% IE) of 59.3, 60.5 and 61.2 % for dibutyltin(IV) 2-nitrobenzoate, 3-nitrobenzoate and 4-nitrobenzoate, respectively. These three dibutyltin(IV) compounds have been shown promising to be potentially used as anticorrosion inhibitors.

Keywords: Inhibitor, Corrosion, Dibutyltin(IV) dinitrobenzoate, Hot rolled plate mild steel.

INTRODUCTION

The interest in the chemistry of organotin compound continues to grow and are mostly due to their significant effects on their biological activity[1,2]. Their biological activities are fundamentally determined by the number and the nature of organic groups bound to the central Sn atom[3]. The nature of the anionic groups seems acting only as a secondary factor[3,4]. The latest researches on the complexation of carboxylate acid derivatives with some organotin(IV) compounds have produced some new organotin(IV) carboxylate derivatives, where in most cases have shown some interesting biological activities such as antimicrobial[5-8], antitumor and anticancer[3,7-11], antifungal activity[4,6,12,13], antiplasmodial[14] and the latest development of these compounds has led to the new finding as anticorrosion inhibitor[15-17], therefore the investigation of organotin(IV) as a prospective anticorrosion is very challenging, has been and will still be attracting more attention.

In the present work, we reported the application and anticorrosion inhibition study of some dibutyltin(IV) dinitrobenzoates toward hot rolled plate mild steel in DMSO-HCl solution.

EXPERIMENTAL

All reagents used were of AR grade. Dibutyltin(IV) dichlorides ([(n-C$_4$H$_9$)$_2$SnCl$_2$]), HCl, dimethyl sulfoxie, sodium hydroxide, 2-nitrobenzoic acid, 3-nitrobenzoic acid and 4-nitrobenzoic acid were obtained from Sigma Aldrich, water HPLC grade, petroleum ether, acetone and methanol were JT Baker products and all of them were used without further purification.

Elemental analyses (CHNS) were performed on Fision EA 1108 series elemental analyser. IR spectra in the range of 4000-300 cm^{-1} were recorded on a Bruker VERTEX 70 FT-IR spectrophotometer with KBr discs. The UV spectra were recorded in the UV region and were measured using a UV- Shimadzu UV-245 Spectrophotometer. Measurements were performed in 1 mL quartz-cells. Solutions were prepared using methanol as the solvent with concentration of 1×10^{-4} M. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 600 MHz NMR (600 MHz for ^{1}H and 150 MHz for ^{13}C). All experiments were run in DMSO-D$_6$ at 298 K. The number of runs used for ^{1}H experiments were 32 with reference at DMSO signal at 2.5 ppm, while the ^{13}C were 1000-4000 scans with the reference DMSO signal at 39.5 ppm.

Synthesis of dibutyltin(IV) dinitrobenzoates: The dibutyltin(IV) dinitrobenzoates used in this work were prepared based on the refinement procedures which have been succesfully used and has been reported previously[10-12]. The following procedure was used in the preparation of dibutyltin(IV) dinitrobenzoate:

To 3.04 g (0.01 mol) [(n-C$_4$H$_9$)$_2$SnCl$_2$] (1) in 50 mL methanol was added 0.8 g (0.02 mol) NaOH. The reaction mixtures were stirred for about 45 min. Compound [(n-C$_4$H$_9$)$_2$SnO] (2) was precipitated out as a white solid, filtered off, washed

succesivelly with double distilled water then with acetone and dried *in vacuo* until it is ready for analysis and further reaction. The average yield was 2.35 g (± 95 %).

To 0.374 g (1.5 mmol) compound **2** in 50 mL of methanol was added with 2 mole equivalents of nitrobenzoic acid (0.25 g) and was refluxed for 4 h at 60-70 °C. After removal of the solvent by rotary evaporator, the solid was washed with petroleum ether (60-80 °C), on cooling a white solid of the product compounds of [(n-C$_4$H$_9$)$_2$Sn(OOCC$_6$H$_4$NO$_2$)$_2$] was obtained and dried *in vacuo* until they are ready for analysis and further use for anticorrosion inhibition test.

Corrosion inhibitor measurement: Mild steel hot rolled plate types were cut in 2 × 1 cm^2 and were successively polished with abrasive paper starting from grid 240, 400, 600 and 800. After the surface of the mild steel were homogenous, the surface were thoroughly washed with distilled water (aquadest), dilute HCl and finally with acetone. The surface area of each mild steel was then measured, weight out and stored in a vacuum desiccator until they were used.

The potentiostat used was ER644 Integrated Potentiostat eDAQ type. It has three electrode cells which is assembly consisted of a working electrode of mild steel (2 cm^2 exposed are), a saturated AgCl as a reference electrode and a platinum counter electrode. After being assembled, they were immersed in corrosive medium as the electrolyte and connected to potentiostat. The first step was the measurement of rate inhibition without inhibitor, all three electrodes were immersed for 10 min in the electrolyte. The potential was set up with scanning rate of 0.5 mV/s. The current change occurred were measured and recorded, the data obtained were then processes to deterimine the potentiodynamic graph (η against ln |j|) in which the current corrosion density (I$_{corr0}$) and corrosion potential (I$_{corri}$) were obtained using Tafel extrapolation method[18]. The similar way was used in the masurement of inhibition rate with inhibitor of dibutyltin(IV) nitrobenzoates. The concentration of inhibitor used were 0, 10, 20, 40, 60, 80 and 100 mg/L. The data in each measurement were recorded and then the percentage of inhibition efficiency (the corrosion rate) were calculated based on eqn. 1.

$$\% \text{ Protection (\% IE)} = \frac{I_{corr_0} - I_{Corr_i}}{I_{corr_0}} \times 100 \% \qquad (1)$$

where % IE: the percentage of inhibition efficiency; I$_{corr_0}$: current before the addition of inhibitor; I$_{corr_i}$: current after the addition of inhibitor.
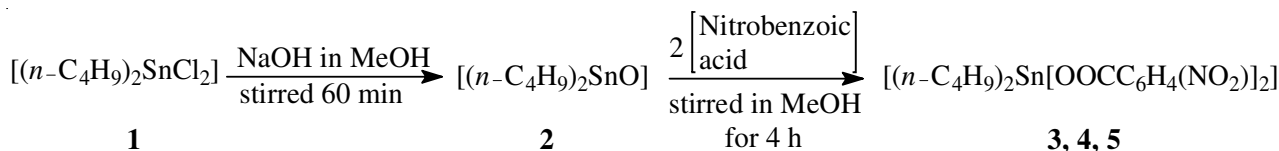
The qualitative analysis of the steel surface was performed by immersing the steel with and without dibutyltin(IV) dinitrobenzoate inhibitor in the corrosive medium and followed by taking the image of the steel surface using microscope after the immersion process.

RESULTS AND DISCUSSION

Synthesis of dibutyltin(IV) dinitrobenzoates: The compounds of dibutyltin(IV) dinitrobenzoate, [(n-C$_4$H$_9$)$_2$Sn(OO-CC$_6$H$_4$NO$_2$)$_2$] (**3**, **4**, **5**), were successfully performed from their chlorides [(n-C$_4$H$_9$)$_2$SnCl$_2$] (**1**), where all of the reactions in all cases were done *via* [(n-C$_4$H$_9$)$_2$SnO] (**2**) similar to those previously reported[10-12]. **Scheme-I** showed the reaction step that occurred in the synthesis of dibutyltin(IV) dinitro-benzate (Fig. 1). Table-1 summarizes the result of microanalytical data of all compounds synthesized and in general the data obtained are good and all values obtained are in aggreement to those of calculated values. The λ$_{max}$ obtained from the UV-visible spectroscopy analyses of all compounds synthesized is summarized in Table-2. It is clear that there was a shifting change in the λ$_{max}$ for each compound in any steps of the reaction and the data agreed to those reported in the literatature[10-12,20,21].

TABLE-2
λ$_{max}$ OF THE UV-VISIBLE SPECTRA OF THE DIBUTYLTIN(IV) COMPOUNDS

Compound	λ$_{max}$ (nm) n-π
[(n-C$_4$H$_9$)$_2$SnCl] (**1**)	210.7
[(n-C$_4$H$_9$)$_2$SnO] (**2**)	202.9
[(n-C$_4$H$_9$)$_2$Sn(o-C$_6$H$_4$(NO$_2$)COO)$_2$] (**3**)	303.2
[(n-C$_4$H$_9$)$_2$Sn(m-C$_6$H$_4$(NO$_2$)COO)$_2$] (**4**)	307.3
[(n-C$_4$H$_9$)$_2$Sn(p-C$_6$H$_4$(NO$_2$)COO)$_2$] (**5**)	301.2

The ^{1}H and ^{13}C chemical shifts of the compounds prepared are shown Table-3. A number of signals in the spectra recorded have been characterized carefully. The chemical shift (δ) of butyl protons attached to the tin metal appeared in the range of 0.92 ppm for Hδ up to 1.37-1.62 ppm for Hα and Hβ and the carbons of butyl ligands are observed at position comparable with other similar compounds reported previously[11,19]. The chemical shift of the carbon from carboxyl group of all compounds as expected appeared in the region of 176-175 ppm and similar to those reported previously and also by other[11,19]. The carbon atoms in the nitrobenzoate ligands appeared in δ

$$[(n\text{-}C_4H_9)_2SnCl_2] \xrightarrow[\text{stirred 60 min}]{\text{NaOH in MeOH}} [(n\text{-}C_4H_9)_2SnO] \xrightarrow[\substack{\text{stirred in MeOH} \\ \text{for 4 h}}]{2\begin{bmatrix}\text{Nitrobenzoic} \\ \text{acid}\end{bmatrix}} [(n\text{-}C_4H_9)_2Sn[OOCC_6H_4(NO_2)]_2]$$

$$\textbf{1} \qquad\qquad\qquad \textbf{2} \qquad\qquad\qquad\qquad \textbf{3, 4, 5}$$

Scheme-I: Scheme of preparative route of the dibutyltin(IV) dinitrobenzoate

TABLE-1
MICROANALYTICAL DATA OF THE DIBUTYLTIN(IV) COMPOUNDS SYNTHESIZED

Compound	Elemental analysis found (calculated)		
	C	H	N
[(n-C$_4$H$_9$)$_2$Sn(o-C$_6$H$_4$(NO$_2$)COO)$_2$] (**3**)	46.30 (46.73)	4.52 (4.60)	4.91 (4.96)
[(n-C$_4$H$_9$)$_2$Sn(m-C$_6$H$_4$(NO$_2$)COO)$_2$] (**4**)	46.23 (46.73)	4.62 (4.60)	4.98 (4.96)
[(n-C$_4$H$_9$)$_2$Sn(p-C$_6$H$_4$(NO$_2$)COO)$_2$] (**5**)	46.41 (46.73)	4.57 (4.60)	4.93 (4.96)

TABLE-3
^{1}H AND ^{13}C CHEMICAL SHIFTS OF THE ORGANOTIN(IV) COMPOUNDS SYNTHESIZED

Compounds	H in butyl (ppm)	H in benzoate (ppm)	C in butyl and benzoate (ppm)
$[(n\text{-}C_4H_9)_2Sn(o\text{-}C_6H_4(NO_2)COO)_2]$ (3)	Hα & Hβ:1.39-1.61 (m); Hγ: 1.29 (m); Hδ: 0.92 (t)	7.34-7.86 (m)	Cα: 21.3; Cβ: 26.6; Cγ: 25.9; Cδ: 14.2; C1: 139.3; C2: 163.3; C3: 130.1; C4: 128.6; C5: 127.1; C6: 129.7; C7: 175.0
$[(n\text{-}C_4H_9)_2Sn(m\text{-}C_6H_4(NO_2)COO)_2]$ (4)	Hα & Hβ:1.4-1.6 (m); Hγ: 1.29 (m); Hδ: 0.93 (t)	7.35-7.89 (m)	Cα: 21.3; Cβ: 26.7; Cγ: 25.9; Cδ: 14.3; C1: 139.3; C2: 131.2; C3: 164.2; C4: 131.2; C5: 129.5; C6: 129.9 C7: 175.2
$[(n\text{-}C_4H_9)_2Sn(p\text{-}C_6H_4(NO_2)COO)_2]$ (5)	Hα & Hβ:1.41-1.6 (m); Hγ: 1.29 (m); Hδ: 0.93 (t)	7.36-7.87 (m)	Cα: 21.3; Cβ: 26.7; Cγ: 25.9; Cδ: 14.2; C1: 139.5; C2: 130.3; C3: 129.1; C4: 164.6; C5: 130.2; C6: 129.9; C7: 175.1

range of 140-130 ppm, thus very close to the reported values for our previous compounds[11].

Table-4 listed the key FT-IR data and the assignments of all functional groups surround tin in every compound were very similar to our previous works[10-12]. The most important characteristic band of the starting material, the compound **1**, is the presence of strong stretching band from Sn-Cl bond which appeared at wave number between 390-310 cm^{-1}. In the compound **1**, the Sn-Cl bond appeared at frequency of 334.2 cm^{-1}. The other characteristic bands of this compound appear as stretching band from butyl ligands at 1069 cm^{-1} and bending vibration of C-H aliphatic stretch of the butyl at frequency of 2956-2865 cm^{-1}. When compound **1** is converted to compound **2**, the main stretching band of Sn-Cl disappeared and a new strong band at frequency of 417.4 cm^{-1} appeared as one of the main stretching band. This band is characteristic for Sn-O bond in compound $[(n\text{-}C_4H_9)_2SnO]$ (**2**). The stretching band due to the butyls and their bending vibrations are still appearing as expected although the frequencies have little bit shifted. The formation of dibutyltin(IV) dinitrobenzoate compounds, $[(n\text{-}C_4H_9)_2Sn(OOCC_6H_4NO_2)_2]$, (**3**, **4**, **5**) is confirmed by the strong asymmetric stretching bands of the carboxylates which occurred at ca. 1400 cm^{-1} and the symmetric stretch at about 1600 cm^{-1} as well as the present of Sn-O stretching of the acid at 435 cm^{-1} and the appearance of these bands is confirming the success of the substitution reaction[10-12].

Anticorrosion inhibition activity test: The increase of inhibition efficiency with increase in inhibitor concentration was observed for all inhibitors (as an example is given in *m*-nitrobenzoic acid series as shown in Fig. 1), a similar observation was also observed by Rastogi *et al.*[15,17]. Based on Fig. 1, it was also noted that the ligands used indeed increased the corrosion activity as shown by their % IE values in which all the ligands used in this work gave negative values. This can be understood that the hydrogen ion of the acid in medium used increasing the number of hygrogen ion due to ionization
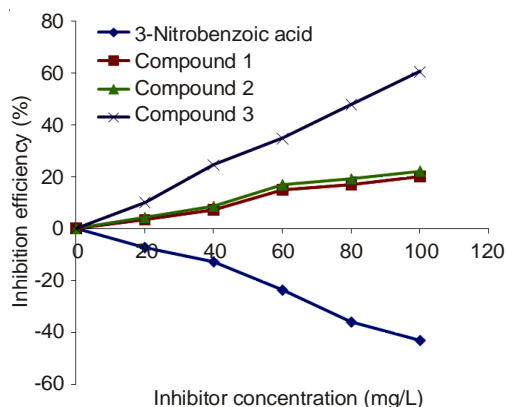

Fig. 1. Comparison curves of %IE *vs* inhibitor concentration

occured to them, as a result all ligands increased the corrosion activity to the mild steel.

All dibutyltin(IV) dinitrobenzoate compounds synthesized exhibited much higher corrosion inhibition activity compared to those of the starting material and intermediate product, as shown in Table-5. In this respect, our results are consistent with a well-known fact that many biologically active compounds become more active upon complexation than in their uncomplexed forms[22].

TABLE-5
PERCENTAGE INHIBITION EFFICIENTY (% IE)

Compounds	% IE
2-Nitrobenzoic acid	-41.9
3-Nitrobenzoic acid	-43.1
4-Nitrobenzoic acid	-42.2
$[(n\text{-}C_4H_9)_2SnCl_2]$ (**1**)	21.9
$[(n\text{-}C_4H_9)_2SnO]$ (**2**)	22.3
$[(n\text{-}C_4H_9)_2Sn(o\text{-}C_6H_4(NO_2)COO)_2]$ (**3**)	59.3
$[(n\text{-}C_4H_9)_2Sn(m\text{-}C_6H_4(NO_2)COO)_2]$ (**4**)	60.5
$[(n\text{-}C_4H_9)_2Sn(m\text{-}C_6H_4(NO_2)COO)_2]$ (**5**)	61.2

TABLE-4
KEY IR BANDS (cm^{-1}) OF THE DIBUTYLTIN(IV) COMPOUNDS

Compound	1	2	3	4	5	Bands
Sn-Cl	334.2	-	-	-	-	390-310
Sn-O	-	417.4	434.6	435.4	435.4	800-400
Sn-Bu	673.4	674.5	675.9	677.1	677.8	740-660
Sn-O-C	-	-	1029.2	1028.8	1028.8	1050-900
butyl	1069.2	1070.9	1073.3	1074.9	1074.1	1100-1060
CO$_2$ asym	-	-	1419.2	1418.4	1418.3	1600-1400
CO$_2$ sym	-	-	1558.2	1560.1	1559.6	1700-1550
C-H aliphatic	2953-2858	2953-2859	2953-2860	2954-2863	2954-2861	2960-2850

According to Crowe[23] the actual biological activity of diorganotin compounds of the type RR'SnXY (R and R' = alkyl or aryl; X and Y = anions) is determined solely by the RR'Sn^{2+} moiety, however the presence of carboxylate or other anions attached to tin metal was proven to be very important in the increased activity of the organotin compounds as it has been observed by many researchers[4-15,17]. Futhermore, it is believed that the organotin(IV) corrosion inhibitors offer an excellent method of protecting various material objects against the aggressive effects of hostile environment, without limitations in regard to shape or size of the object to be protected[16]. It has been shown by qualitative analysis by immersing the mild steel into the solution containing inhibitor dibutyltin(IV) compared to immersing the mild steel into corrosive medium withoug inhibitor (Fig. 2). The careful observation of the steel surface with microscope was clearly indicated that the corrosion in the surface of the mild steel which was immersed with corrosive medium without inhibitor did occur as shown by the formation of holes on the surface which is known as wells corrosion[24] (Fig. 2a). The addition of dibutyltin(IV) dinitrobenzoate into the corrosive medium used significantly inhibit the corrosion process as shown by the less formation of wells corrosion (Fig. 2b). Therefore, corrosion protection is offered by partial or complete inhibition of the electrochemical reactions[16].
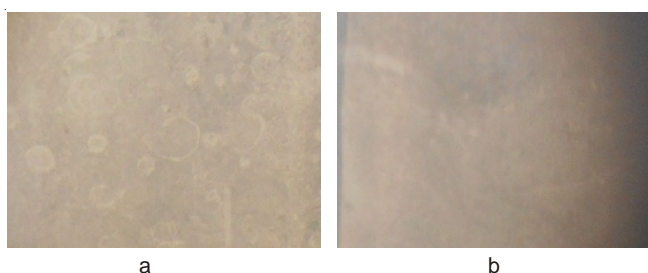

a   b

Fig. 2. Surface of mild steel (a) corrosive medium without inhibitor and (b) corrosive medium with the addition of dibutyltin(IV) di-3-nitrobenzoate

Conclusion

The dibutyltin(IV) dinitrobenzoate were continued to be successfully prepared and it was quite clear that they have shown some promising results to be used as anticorrosion inhibitor. Although they are not as strong as other related derivatives of organotin(IV). However, they are still good to be used as anticorrosion inhibitors. Further studies are being carried out to find the best inhibitor and the better way to apply these compounds and other derivatives for the new generation of anticorrosion which will be useful for many industries.

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