



The anticorrosion activity of dibutyltin(IV) and diphenyltin(IV) dihydroxybenzoate compounds towards HRP mild steel in NaCl

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ABSTRACT

In this paper, we reported syntheses of 6 compounds of a series of dibutyltin(IV) and diphenyltin(IV) dihydroxybenzoate compounds which have successfully been prepared from the starting materials of dibutyltin(IV) dichloride and diphenyltin(IV) dichloride respectively via the intermediate products of dibutyltin(IV) oxide and diphenyltin(IV) dihydroxide with o-, m-, and p-hydroxybenzoic acids. The new compounds synthesized were well characterized by ^1H and ^{13}C NMR, IR and UV-Vis spectroscopies as well as based on the microanalytical data. The anticorrosion activities of these compounds were tested toward HRP mild steel in NaCl medium using potentiodynamic methods. The results indicated that the diphenyltin(IV) compounds showed much better activity than those of dibutyltin(IV) analogous. The results obtained indicated that the higher anticorrosion activities were observed to depend on the nature of the ligand attached to the Sn centre. The number of carbon atoms present in the ligands attached to the metal center might also play an important role.

Keywords: corrosion inhibitor, mild steel, NaCl medium, organotin(IV) hydroxybenzoate

INTRODUCTION

The organotin(IV) compounds continue to attract many chemists because of their strong effect in many biological tests [1-2]. The main factor affecting their biological activities is determined by the number and the organic groups attached to Sn center [3], while the present and the nature of the anionic groups is only as a secondary factor [3-4]. The investigations on the coordination of carboxylates and their derivatives into organotin(IV) compounds have led to the isolation of some new organotin(IV) carboxylates and carboxylate derivatives which 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 the new finding as new anticorrosion inhibitor [15-19], therefore the investigation of organotin(IV) carboxylate as possible corrosion inhibitor is still very challenging, thus much attention is still given in this area [15-19].

Corrosion is an electrochemical reaction that occurred naturally, so the corrosion reaction can proceed by itself, as a result it cannot totally be stopped [20,21]. However, it might be controlled or slow down its rate as to decrease the corrosion process [22]. One of the methods offered to slow down the corrosion process is by the use of inhibitor. Corrosion inhibitor is a chemical compounds which can protect or slow down the corrosion process [15-19, 22].

Based on the fact that organotin(IV) carboxylate compounds have been found to have a promising result as inhibitor corrosion, in this paper, we reported the application and anticorrosion inhibition study of some dibutyltin(IV) and diphenyltin(IV) dihydroxybenzoate toward mild steel hot roller plate (HRP) in NaCl.

EXPERIMENTAL SECTION

All reagents used were AR grade. Dibutyltin(IV) dichlorides ($[(n\text{-C}_4\text{H}_9)_2\text{Cl}_2]$), diphenyltin(IV) dichloride ($[(\text{C}_6\text{H}_5)_2\text{Cl}_2]$), 2-hydroxybenzoic acid, 3-hydroxybenzoic acid and 4-hydroxybenzoic acid, NaCl were obtained from Sigma, water HPLC grade, sodium hydroxide (NaOH) and methanol (CH_3OH) were JT Baker products, and were used without further purification.

Characterization

Microelemental analyses (CHNS) were performed on Fision EA 1108 series elemental analyzer. IR spectra in the range of $4000\text{-}400\text{cm}^{-1}$ 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 $1.0 \times 10^{-4}\text{M}$.

^1H and ^{13}C NMR spectra were recorded on a Bruker AV 600 MHz NMR (600 MHz for ^1H and 150 MHz for ^{13}C). All experiments were run in DMSO-D_6 at 298K. The number of runs used for ^1H 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.

Preparation of organotin(IV) dihydroxybenzoate

The organotin(IV) dihydroxybenzoate used in this work were prepared based on the procedure previously reported [10-12,18-19] and was adapted from the work by Szorcsik *et al.* [6]. For example the procedure in the preparation of dibutyltin(IV) dihydroxybenzoate was as follows:

To 3.0383 g (0.01 mol) $[(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2]$ in 50 mL methanol was added 0.8 g (0.02 mol) NaOH. The reaction mixtures were stirred for about 45 minutes. Compound **2** was precipitated out as white solid, filtered off and dried *in vacuo* till they are ready for analysis and further reaction. The average yield was 2.33 g (94 %).

To 0.37338 g (1.5 mmol) compound **2** in 50 mL of methanol was added with 2 mole equivalents of hydroxybenzoic acid (0.2505 g) and was refluxed for 4 hours at $60 - 70^\circ\text{C}$. After removal of the solvent by rotary evaporator, the produced compounds $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OOC}\text{C}_6\text{H}_4\text{OH})_2]$ were dried *in vacuo* until they are ready for analysis and further use for corrosion inhibition test. The average yields were more than 90 %.

A similar procedure was also adapted in the preparation of diphenyltin(IV) dihydroxybenzoate, $[(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OOC}\text{C}_6\text{H}_4\text{OH})_2]$.

Corrosion inhibitor measurement

The method used for this experiment is based on the procedure successfully applied in our previous works [18, 19] and as follows:

Mild steel hot roll plate types were cut in $2 \times 1\text{ cm}^2$ 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 minutes 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 determine 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, 19]. The similar way was used in the measurement of inhibition rate with inhibitor of organotin(IV) hydroxybenzoate. The concentrations 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) was calculated based on Equation 1.

$$\% \text{ protection } (\%IE) = \frac{I_{corr0} - I_{corri}}{I_{corr0}} \times 100\% \dots \dots \dots (1)$$

Where %IE: the percentage of inhibition efficiency; I_{corr0} : current before the addition of inhibitor; I_{corri} : current after the addition of inhibitor

RESULTS AND DISCUSSION

Continuing the success in the preparation of the organotin(IV) carboxylate compounds in all our previous works [10-12,18,19], we have been successful in the preparation and characterization of dibutyltin(IV) dihydroxybenzoate, $[(n-C_4H_9)_2Sn(OOCC_6H_4OH)_2]$ (**3** - **5**) and diphenyltin(IV) dihydroxybenzoate, $[(C_6H_5)_2Sn(OOCC_6H_4OH)_2]$ (**8-10**). They were successfully prepared from their chlorides $[(n-C_4H_9)_2SnCl_2]$ (**1**) and $[(C_6H_5)_2SnCl_2]$ (**6**), respectively, where all of these reactions were performed *via* $[(n-C_4H_9)_2SnO]$ (**2**) and $[(C_6H_5)_2Sn(OH)_2]$ (**7**) respectively similar to those previously reported [10-12,18,19]. An example of the reaction step that occurred in the preparation of dibutyltin(IV) dihydroxybenzoate is shown in Fig. 1. The proposed structure and numbering of the carbon in the compounds synthesized is shown in Fig. 2. The data of microanalysis for all compounds synthesized are tabulated in Table 1 and in general all values obtained are very good and are close to the calculated theoretical values.

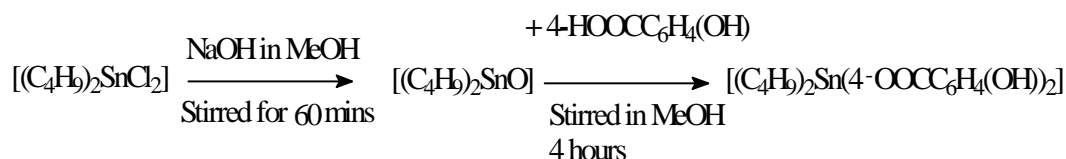


Figure 1. The scheme of preparative route of the organotin(IV) dihydroxybenzoate

Table 1. The microanalytical data of the organotin(IV) compounds synthesized

Compound	Elemental analysis found (calculated)	
	C	H
$[(n-C_4H_9)_2Sn(o-C_6H_4(OH)COO)_2]$ (3)	51.8 (52.1)	5.7 (5.6)
$[(n-C_4H_9)_2Sn(m-C_6H_4(OH)COO)_2]$ (4)	52.1 (52.1)	5.7 (5.6)
$[(n-C_4H_9)_2Sn(p-C_6H_4(OH)COO)_2]$ (5)	52.3 (52.1)	5.8 (5.6)
$[(C_6H_5)_2Sn(o-C_6H_4(OH)COO)_2]$ (8)	56.3 (57.0)	3.6 (3.7)
$[(C_6H_5)_2Sn(m-C_6H_4(OH)COO)_2]$ (9)	56.9 (57.0)	3.7 (3.7)
$[(C_6H_5)_2Sn(p-C_6H_4(OH)COO)_2]$ (10)	57.1 (57.0)	3.7 (3.7)

Some spectroscopy techniques have been utilized to characterize all compounds synthesized. The important FT-IR data and their assignments are presented in Table 2. The presence of C=O peak in the range of 1600-1400 cm^{-1} in 6 organotin(IV) dihydroxybenzoate synthesized was an indication that hydroxybenzoic acid has been bound to metal center Sn. In the region of 3500 - 3200 cm^{-1} in all compounds, there was a broad peak indicated the presence of -OH group. The other characteristic stretch of the products was for Sn-O in the region of 800-600 cm^{-1} . The evidence of the bound of hydroxybenzoate to the Sn in compound **8** - **10** was the strong vibration bend at 592.3, 593.1, and 594.7 cm^{-1} , respectively which indicated that the substitution of -OH in **8-10** has taken place [10-12,18-19].

Table 2. The characteristic and important IR bands of the organotin(IV) compounds (cm^{-1}) synthesized

Compound	3	4	5	8	9	10	References
Sn-O	479.2	477.4	477.4	592.3	593.1	594.7	600-400
Sn-O-C	1053.1	1051.8	1048.8	1242.2	1250.4	1260.4	1290-1000
Sn-Bu	748.1	778.7	781.3	-	-	-	800-660
CO ₂ asym	1429.2	1428.4	1421.4	1531.7	1536.2	1546.3	1600-1400
CO ₂ sym	1595.5	1560.1	1557.2	1661.2	1670.3	1672.3	1700-1550
C-H aliphatic	2929 - 2860	2951 - 2863	2954 - 2856	-	-	-	2960 - 2850
Phenyl	-	-	-	1468.2; 752.1	1490.5; 725.7	1490.5; 725.7	1450, 730
-O-H	3441.7	3440.9	3439.3	3447.8	3447.8	3449.8	3500-3100

The UV-Vis spectroscopy analyses of all the compounds have also been performed to obtain the λ_{max} . The data obtained are shown in Table 3. It is clear that there was some important shifting change in the λ_{max} for each compound in any steps of the reaction. In the spectra, all synthesized compounds produced 2 peaks due to transition of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. For example in compounds **1** and **2**, the λ_{max} observed were 210.7 and 202.9 nm respectively, while the $n \rightarrow \pi^*$ transition did not appear. In **3**, **4**, **5**, there were large shift in the $\pi \rightarrow \pi^*$ transition, at the same time due to the bound of hydroxybenzoate to the compounds synthesized, the $n \rightarrow \pi^*$ transitions were observed for all compounds. The bathochromic shift from the starting material to the synthesized

Table 4. ¹H and ¹³C spectra of the compounds synthesized

Compounds	H in butyl or phenyl (ppm)	H in benzoate (ppm)	C in butyl, phenyl and benzoate (ppm)
[(<i>n</i> -C ₄ H ₉) ₂ Sn(<i>o</i> -C ₆ H ₄ (OH)COO) ₂] (3)	H α & H β : 1.37-1.62 (m); H γ : 1.29 (m); H δ : 0.92 (t)	7.34-7.86 (m)	C α : 21.3; C β : 26.6; C γ : 25.9; C δ : 14.2; C1: 174.9; C2: 139.3; C3 & C7: 129.7; C4 & C6: 128.6; C5: 125.1
[(<i>n</i> -C ₄ H ₉) ₂ Sn(<i>m</i> -C ₆ H ₄ (OH)COO) ₂] (4)	H α & H β : 1.38-1.62 (m); H γ : 1.30 (m); H δ : 0.93 (t)	7.35-7.89 (m)	C α : 21.3; C β : 26.7; C γ : 25.9; C δ : 14.3; C1: 175.2; C2: 139.3; C3: 130.1; C4: 164.6; C5: 129.5; C6: 128.9; C7: 129.9
[(<i>n</i> -C ₄ H ₉) ₂ Sn(<i>p</i> -C ₆ H ₄ (OH)COO) ₂] (5)	H α & H β : 1.4-1.62 (m); H γ : 1.31 (m); H δ : 0.93 (t)	7.36-7.89 (m)	C α : 21.4; C β : 26.8; C γ : 25.9; C δ : 14.4; C1: 175.1; C2: 139.6; C3: 130.3; C4: 164.8; C5: 129.9; C6: 129.2; C7: 129.9
[(C ₆ H ₅) ₂ Sn(<i>o</i> -C ₆ H ₄ (OH)COO) ₂] (8)	H2 & H6 7.56 (d, 4H); H3 & H5 7.48 (t, 4H); H4: 7.35 (t, 2H)	7.81-7.93 (m)	C1-6 (phen): 131.7-126.9; C7: 175.7; C8: 139.5; C9 & C13: 130.2; C10 & C12: 129.1; C11: 128.5
[(C ₆ H ₅) ₂ Sn(<i>m</i> -C ₆ H ₄ (OH)COO) ₂] (9)	H2 & H6 7.58 (d, 4H); H3 & H5 7.48 (t, 4H); H4 7.36 (t, 2H)	7.84-7.95 (m)	C1-6 (phen): 131.7-126.8; C7: 175.8; C8: 139.3; C9: 130.8; C10: 164.7; C11: 129.7; C12: 129.0; C13: 130.2
[(C ₆ H ₅) ₂ Sn(<i>p</i> -C ₆ H ₄ (OH)COO) ₂] (10)	H2 & H6 7.59 (d, 4H); H3 & H5 7.50 (t, 4H); H4 7.37 (t, 2H)	7.89-7.99 (m)	C1-6 (phen): 131.7-126.9; C7: 175.9; C8: 139.8; C9: 130.4; C10: 164.9; C11: 129.9; C12: 129.4; C13: 130.3

We have reported previously that in the antifungal and anticancer activity study of similar compounds reported here [11-12], their activities were associated with the number of carbon atoms of the ligand present in the organotin(IV) used [10-12,18,25]. Based on the result shown in Table 5, the diphenyltin(IV) derivatives were shown to inhibit stronger than those of dibutyltin(IV) compounds, a similar observation to the result obtained in our previous work [18,19]. Thus the number of carbon atoms present in the ligands used as well as the type of the ligands themselves played significant role in the anticorrosion activity study. Furthermore, the previous anticorrosion activity studies of similar compounds were reported using DMSO-HCl solution as the media [18,19], in this work, we have utilized salt medium for the anticorrosion test. The results observed, surprisingly, close to the result of previous work and are in the same line as shown in Table 5.

Table 5. The percentage of inhibition efficiency

Compounds	% IE
2-hydroxybenzoic acid	-19.7
3-hydroxybenzoic acid	-18.9
4-hydroxybenzoic acid	18.1
[(<i>n</i> -C ₄ H ₉) ₂ SnCl ₂]	21.9
[(<i>n</i> -C ₄ H ₉) ₂ SnO]	22.3
[(<i>n</i> -C ₄ H ₉) ₂ Sn(<i>o</i> -C ₆ H ₄ (OH)COO) ₂] (3)	59.2
[(<i>n</i> -C ₄ H ₉) ₂ Sn(<i>m</i> -C ₆ H ₄ (OH)COO) ₂] (4)	58.5
[(<i>n</i> -C ₄ H ₉) ₂ Sn(<i>p</i> -C ₆ H ₄ (OH)COO) ₂] (5)	58.1
[(C ₆ H ₅) ₂ Sn(<i>o</i> -C ₆ H ₄ (OH)COO) ₂] (8)	78.2
[(C ₆ H ₅) ₂ Sn(<i>m</i> -C ₆ H ₄ (OH)COO) ₂] (9)	77.9
[(C ₆ H ₅) ₂ Sn(<i>p</i> -C ₆ H ₄ (OH)COO) ₂] (10)	77.1

We also observed that all organotin(IV) dihydroxybenzoate compounds synthesized have shown much higher corrosion inhibition compared to those of the ligands, starting materials and intermediate products. 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 [25]. According to Crowe [27] 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'Sn²⁺ moiety.

CONCLUSION

The preparation of organotin(IV) dihydroxybenzoate compounds were successfully achieved and it is clear from the result obtained that they are potentially to be used as new anticorrosion inhibitor. The diphenyltin(IV) dihydroxybenzoate derivatives have shown to have higher anticorrosion ability, these observations were similar with other data that the number of carbon atom of the ligands attached to the compounds have strong effect to the anticorrosion activity. It might also relate to the ability of phenyl ligand to draw electron from the metal center as a result the metal became more positive and attached strongly to the steel and protect the steel from corrosion in the corrosive medium. The other related works using a variety of compounds are still on progress and will be reported elsewhere.

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