

Square Wave Voltammetric Analysis of Triphenyltin(IV) Hydroxybenzoate Derivatives

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In present work, a chemical analysis of two newly synthesized compounds, triphenyltin(IV) *o*-hydroxybenzoate (**1**) and triphenyltin(IV) *m*-hydroxybenzoate (**2**) have been performed by using square wave voltammetry (SWV). The method used was validated using the standard solutions of compound **1** and **2** by varying the concentrations. The concentrations of 1.6×10^{-4} M; 3.2×10^{-4} M; 4.8×10^{-4} M; 6.4×10^{-4} M and 8.0×10^{-4} were used in the variations. The validation results of compound **1** were the linear regression equation: $i_p = 7.42 C + 7.89$; correlation coefficient (r) = 0.991; limit of detection (LOD) = 1.53×10^{-4} M; and sensitivity (S) = 7.42 μ A/ mM, while compound **2** gave the value of linear regression equation: $i_p = 8.39 C + 7.91$; correlation coefficient (r) = 0.991; limit of detection (LOD) = 1.35×10^{-4} M; and sensitivity (S) = 8.39 μ A/mM.

Keywords: Square wave voltammetry, Triphenyltin(IV) *o*-hydroxybenzoate, Triphenyltin(IV) *m*-hydroxybenzoate.

INTRODUCTION

The application of electroanalytical techniques to pharmaceutical and biomedical analysis has grown vastly in recent decade as biological reactions in human beings and electrochemical reactions at solution-electrode interface follow same set of electron transfer pathways. Many important physiological, enzymatic and other biochemical processes work on principle of electrochemical oxidation/reduction mechanism [1,2].

The organotin(IV) and their derivatives continue to attract much attention due to their attractive biological activities [3-8]. Due to excess usage of the highly toxic organotin(IV) compounds in various fields, humans are exposed to organotins not solely through ingestion of contaminated seafood but also through direct contact with treated products and by inhalation and ingestion of dust, thus the scientific community and the health organizations at local and international level, to a systematic research for the precise and accurate determination of these compounds, even at very low concentrations in the environment [9,10].

Because of the large differences in the bioavailability and toxicity of these organotin species, several analytical approaches have been used for their accurate and precise determination in ultratrace concentrations in environmental samples, such

as sediments, marine organisms or surface waters. The organotin analysis is a multi-step procedure and mostly sophisticated techniques have been reported [11-17]. In most of the techniques an additional step, derivatization of the organotin species to more volatile compounds is required, such as hydride generation or Grignard alkylation [18]. Moreover, in several cases no differentiation of organotins is possible and necessary to be converted into inorganic tin prior to their polarographic determination.

Subsequently a very low environmental quality standards are set internationally for organotin compounds, thus fulfilment of these regulatory demands has necessitated the development of highly sensitive and selective analytical techniques for the measurement of these compounds. In the present work, the electrochemical behaviour of two organophenyltin (IV) compounds *viz.* triphenyltin(IV) *o/m*-hydroxybenzoates by square wave voltammetric technique was carried out.

EXPERIMENTAL

Two organotin(IV) compounds *viz.* tri-phenyltin(IV) *o*-hydroxybenzoate (**1**) and triphenyltin(IV) *m*-hydroxybenzoate (**2**) used for analysis in the present work were synthesized according to the previous method [19]. For the extraction of

the organotin compounds, dichloromethane, p.a., sodium chloride and absolute ethanol (Merck) were obtained from Merck and used without further purification. ER644 integrated potentiostat eDAQ with three electrode system was used, which consist of gold electrode as working electrode, silver wire as pseudo-reference electrode and platinum as counter electrode.

Preparation of solution (10^{-3} M): The solution stocks for compounds **1** and **2** were prepared as described earlier [19].

Preparation of supporting electrolyte (NaCl) solution: Stock solution of NaCl (0.1 N), which is used as the supporting electrolyte was prepared by dissolving 29.25 mg of NaCl in 50 mL water in volumetric flask. Further aliquots were prepared by serial dilution.

Blank solution measurement with square wave voltammetry: A DMSO (2.5 mL) and water (7.5 mL) was mixed in a volumetric flask and stirred until the mixture become homogeneous. Then the measurement was carried out by taking 2 mL of blank solution in 250 mL Erlenmeyer flask and 0.5 mL NaCl (0.02N) as supporting electrolyte was added to the blank solution. The voltammogram was run with potential range of +700 mV to +1400 mV.

Voltammetric measurements: A 10 mL of analyte (triphenyltin(IV) *o*-hydroxybenzoate and triphenyltin(IV) *m*-hydroxybenzoate) having concentrations variation of 1.6×10^{-4} M; 3.2×10^{-4} M; 4.8×10^{-4} M; 6.4×10^{-4} M and 8.0×10^{-4} M was transferred into the microelectrolysis cell and then deoxygenated with pure nitrogen gas before measurements while a stream of nitrogen gas was kept over surface of the solution in the electrolysis cell during the measurements. Pre-concentration of the analyte onto surface of the HMDE was carried out by adsorptive accumulation at -0.05 V (*vs.* Ag/AgCl/KCl) for 120 s while stirring the solution at 400 rpm. After elapsed the accumulation time, the stirrer was stopped and a 5 s rest period was allowed for the solution to become quiescent. Voltammograms were recorded by scanning the potential towards the negative direction using square wave potential-waveform. Quantification of triphenyltin(IV) *o*-hydroxybenzoate (**1**) or triphenyltin(IV) *m*-hydroxybenzoate (**2**) was performed by means of both calibration curve and standard addition methods.

Statistical analysis: The data which were obtained from measurement were then subjected for evaluation by some statistical parameters using the method available in literature [20].

RESULTS AND DISCUSSION

A square wave adsorptive anodic stripping voltammetric measurements were carried out with the ER644 integrated potentiostat eDAQ with three electrode system, which consist of gold electrode as working electrode, silver wire as pseudo-reference electrode and platinum as counter electrode. The voltammogram of standard solution *i.e.* triphenyltin(IV) *o/m*-hydroxybenzoates are shown in Fig. 1.

The voltammograms of compounds **1** and **2** were obtained as results of increasing the oxidation potential by the voltammogram, thus the anodic peak current (i_p) and anodic peak potential (E_p) can be identified. The data of i_p and E_p values of the standard solution are shown in Table-1 for different concentration.

The results shown in Table-1 indicated that the oxidation current peak increases as the concentration increased [21]. Accordingly, it is observed that the obtained potential scan rate and the peak current are related proportionally.

Furthermore, the values of peak potential obtained for blank solution must be different respective to the standard solution. In order to make sure about E_p values, the statistical test using the hypothesis test (F-test) has been applied. The hypothesis is accepted if $F_{calc.} < F_{found.}$ Based on the test result, it was found that $F_{calc.} > F_{found.}$ which means that the E_p values between the standard solution and blank solution have significant differences, so it can be said that the samples analyzed were not from the similar kind of samples.

Some validation methods have been applied to validate the obtained data. The relationship between the concentration and the current produced was evaluated using a good linear correlation which were obtained from the calibration curve (Fig. 2). The parameters of the concentration-current straight line were calculated by the least squares method.

The regression linear of triphenyltin(IV) *o*-hydroxybenzoate (**1**) was $y = 7.42x + 7.89$ or $i_p = 7.42 C + 7.89$ with coefficient correlation (r) of 0.992 and for triphenyltin(IV) *m*-hydroxybenzoate (**2**), the regression linear obtained was $y = 8.39x + 7.91$ or $i_p = 8.39 C + 7.91$ with coefficient correlation (r) of 0.991. Thus, the technique utilized in this study is able to be applied to evaluate the organotin(IV) derivatives with sensitivity of triphenyltin(IV) *o*-hydroxybenzoate (**1**) and triphenyltin(IV) *m*-hydroxybenzoate (**2**) were $7.42 \mu\text{A}/\text{mM}$ and $8.39 \mu\text{A}/\text{mM}$, respectively.

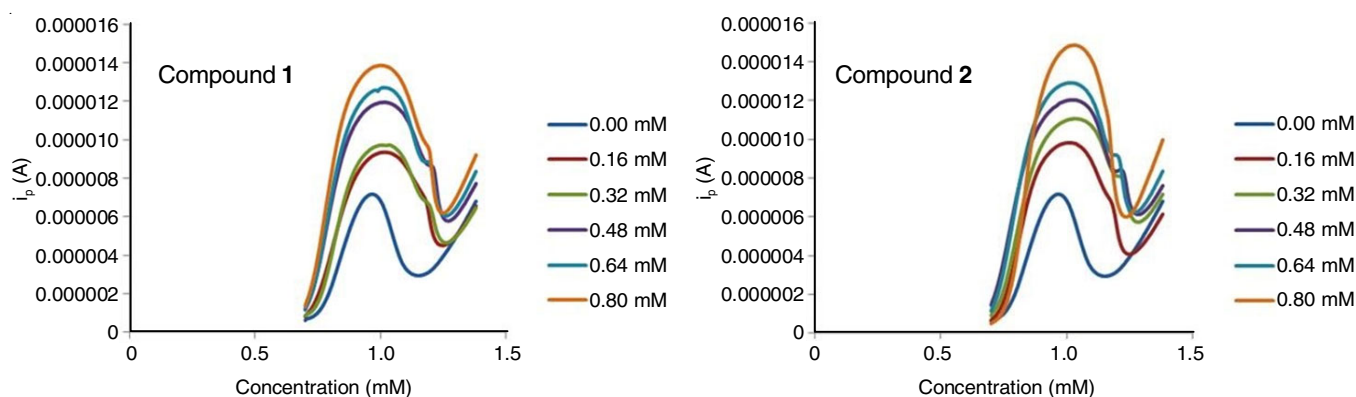


Fig. 1. Voltammograms of compounds **1** and **2** at various concentrations using square wave voltammetry

TABLE-1
THE i_p AND E_p VALUES OF STANDARD SOLUTION OF COMPOUNDS 1 AND 2

S. No.	0 M		1.6×10^{-4} M		3.2×10^{-4} M		4.8×10^{-4} M		6.4×10^{-4} M		8.0×10^{-4} M	
	Comp. 1	Comp. 2	Comp. 1	Comp. 2	Comp. 1	Comp. 2	Comp. 1	Comp. 2	Comp. 1	Comp. 2	Comp. 1	Comp. 2
E_p (Volt)												
1	0.97	0.97	1.01	1.02	1.01	1	1.01	1.015	1.01	1.015	1	1.03
2	0.97	0.97	1.01	1.02	1.025	1	1.01	1.015	1.005	1.015	1	1.03
3	0.975	0.975	1.005	1.01	1.025	1.02	1.005	1.015	1.01	1.02	1	1.03
4	0.975	0.975	1.015	1.01	1.01	1.03	1.02	1.025	1.01	1.015	1	1.03
5	0.975	0.975	1.01	1.015	1.015	1.03	1.02	1.02	1.01	1.015	1	1.03
Mean	0.97	0.97	1.01	1.015	1.017	1.016	1.013	1.018	1.009	1.016	1	1.03
RSD (%)	0.3	0.3	0.350	0.493	0.746	1.493	0.662	0.439	0.222	0.220	0	0
i_p (μ A)												
1	7.17	7.17	9.35	9.56	9.82	9.95	11.72	11.9	12.62	12.66	13.5	14.86
2	7.45	7.45	9.4	9.68	9.9	10.05	11.72	11.9	12.66	12.67	13.58	14.93
3	7.72	7.72	9.44	9.7	9.91	10.82	11.85	11.93	12.67	12.82	13.6	14.96
4	7.92	7.92	9.44	9.78	9.92	10.84	11.92	11.99	12.68	12.88	13.69	14.97
5	8.13	8.13	9.46	9.82	9.95	11.07	11.95	12.03	12.71	12.97	13.87	14.99
Mean	7.678	7.678	9.418	9.708	9.9	10.546	11.832	11.95	12.668	12.8	13.648	14.942
RSD (%)	4.9	4.9	0.465	1.036	0.489	4.829	0.917	0.484	0.258	1.049	1.035	0.339

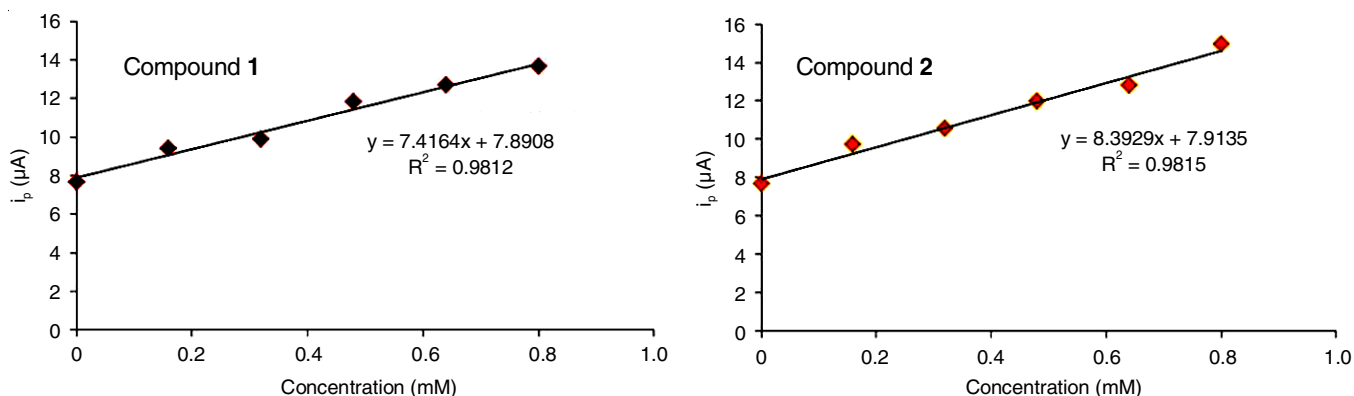


Fig. 2. Calibration curves of compounds 1 and 2 using square wave voltammetry

The proximity of the result of independent test which was obtained under the experimental conditions is related to precision. The method which gives a good precision is indicated by the relative standard deviation (RSD) of less than 5% value [20]. The results of analysis on the blank solution produced the RSD values for both compounds which were below 5%, *i.e.* 3.16% and 3.43%, therefore the RSD for both standard solutions used in this work were categorized as good. The results of limit of detection for the instrument that has been used in the measurement is presented in Table-2 and the results are very good in term of giving RSD below the standard and very low LOD.

Selectivity: The needs of method validation in the analysis carried out were not only to make sure the validity, but also to

prove that the method applied was appropriate for the analysis. The analysis procedure of must be able to show the small changes in concentration which relates to the sensitivity. It is counted as the ratio of voltage increase associating with the increase of each analyte concentration [20]. The result of regression linear from the experiment carried out, the sensitivity for both compounds were 3.161% and 3.426%, respectively indicating that the sensitivity values for both compounds corresponded to the slope on the obtained regression linear equation.

Conclusion

The present work describes a validated square wave adsorptive anodic stripping voltammetric analysis of triphenyltin(IV) *o*-hydroxybenzoate (1) and triphenyltin(IV) *m*-hydroxyben-

TABLE-2
THE REGRESSION PARAMETER VALUES OF COMPOUNDS 1 AND 2

S. No.	Standard Solution	r	Sensitivity (μ A/mM)	RSD (%)	LoD (mM)
1	Triphenyltin(IV) <i>o</i> -hydroxybenzoate	0.991	7.46	3.16	1.53
2	Triphenyltin(IV) <i>m</i> -hydroxybenzoate	0.991	8.39	3.43	1.35
3	Triphenyltin(IV) <i>p</i> -hydroxybenzoate [Ref. 19]	0.995	6.19	1.97	1.84
4	Triphenyltin(IV) benzoate [Ref. 20]	0.995	2.07	2.97	4.09

zoate (**2**) without interference from common excipients. Hence, it could be applied for the routine quality control of the studied drug either in bulk or in its corresponding dosage forms.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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