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Electrochemical Behavior of Dibutyltin(IV) Compounds and Their Determination at ppb Levels by Differential Pulse Anodic Stripping Voltammetry

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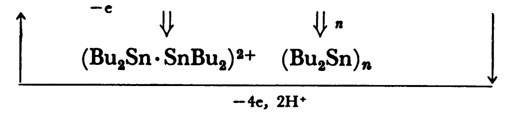
The electrochemical behavior of dibutyltin(IV) compounds (Bu_2SnX_2) (X=chloride, laurate (L), and 6-methylheptyl maleate (MHM)) in 50% (v/v) and 80% (v/v) ethanol–water media (apparent pH 7.3) containing 0.002% Triton X-100 has been investigated by polarography and cyclic voltammetry. It has been found that Bu_2SnX_2 gives a two-electron transfer step at about −0.8 V *vs.* SCE, which consists of very close two one-electron steps, and a two-electron step at about −1.4 V in both media. Over the potential range of either side of the first reduction wave, both Bu_2SnX_2 and their reduction products are significantly adsorbed on the surface of a mercury electrode in 50% (v/v) ethanol, but not in 80% (v/v) ethanol. The adsorbed reduction products are readily re-oxidized at the mercury electrode in 50% ethanol. The re-oxidation peak was successfully utilized for the determination of traces of Bu_2SnCl_2 by means of the differential pulse anodic stripping voltammetry (DPASV) over the concentration range of 3—50 ppb (μg dm^{-3}) at the deposition time of 60 s. The DPASV behavior of Bu_2SnX_2 (X=chloride, L, MHM, and 1-dodecanethiolate) has been investigated in a 50% ethanol medium in detail. Further, a procedure has been developed for determining Bu_2SnX_2 in natural water down to ppb levels.

In recent years, organotin compounds attained rapidly commercial importance. Dibutyltin compounds are widely used as stabilizers for PVC plastics and as the control of helminthic and protozoal infections in poultry.[1] Various methods have been proposed for the determination of organotin compounds, *e.g.* atomic absorption spectrophotometry,[2,3] and fluorometry.[4] As the organotin compounds are reduced at a dropping mercury electrode (DME), this offers the possibility of direct determination.[5–14] Triphenyltin chloride (Ph_3SnCl)[5] and tributyltin compounds[6] are strongly adsorbed onto the electrode surface when reduced at the mercury electrode to the corresponding radicals. This property has been utilized for the determination of traces of Ph_3SnCl and tributyltin compounds by anodic stripping voltammetry (ASV).[5,7,8] Polarographic behavior of dialkyl- and diaryltin(IV) compounds (R_2SnX_2)(R=methyl, ethyl, butyl, phenyl, and X=anion) was also investigated in acids, ethanol–water, *etc.*[9–14] Fleet and Fouzder[11] showed that dibutyltin compounds (Bu_2SnX_2)(X=laurate (L) and maleate (M)) in the 80% (v/v) ethanol–water medium (pH 7.0) gave three reduction waves and proposed the following mechanism.



$$\begin{tikzcd}
\text{step 1} & \text{step 2} & \text{step 3} & \\
Bu_2Sn^{2+} \arrow[r, shift left, "+e"] & Bu_2Sn^{\dot{+}} \arrow[l, shift left, "-e"] \arrow[r, "+e"] \arrow[d, Rightarrow] & Bu_2Sn: \arrow[r, "2e.\ 2H_2O"] \arrow[d, Rightarrow, "n"] & Bu_2SnH_2 \arrow[lll, bend left=60, "-4e,\ 2H^+"] \\
 & (Bu_2Sn\cdot SnBu_2)^{2+} & (Bu_2Sn)_n &
\end{tikzcd} \quad (1)$$

In this mechanism they, however, claimed that no adsorption of both depolarizers and their reduction products occurred at the surface of a mercury electrode. Morris[9] studied the polarographic behavior of diethyltin compounds (Et_2SnX_2) in aqueous acid solutions and claimed that a reversible two-electron step distorted by the formation of insoluble polymer products ($(Et_2Sn)_n$) was observed on the electrode surface. We have investigated the polarographic behavior of Bu_2SnCl_2 in the 50% (v/v) ethanol–water medium (pH 7.3) containing 0.002% Triton X-100, a surface-active agent, as a maximum suppressor. Contrary to the previous work by Fleet and Fouzder[11] described above, significant adsorption has been found of both depolarizer and its reduction product(s) onto the mercury electrode, and the adsorbed reduction product(s) is readily re-oxidized. These findings has been successfully utilized for the determination of traces of Bu_2SnCl_2 by differential pulse anodic stripping voltammetry (DPASV) which is one of the most sensitive electrochemical techniques for trace analysis. Meanwhile there have been few reports on the ASV of dibutyltin compounds.

In this paper, we present a more detailed electrochemical behavior of Bu_2SnX_2 (X=chloride, L, and 6-methylheptyl maleate (MHM)) at the mercury electrode in the same medium as described above, primarily with the aim of developing a more sensitive method, *i.e.* DPASV, of Bu_2SnX_2 (X=chloride, L, MHM, and 1-dodecanethiolate (DT)).

Experimental

Materials. The following tin compounds were used in this study: Bu_2SnCl_2, Ph_3SnCl (Tokyo Kasei Kogyo, Tokyo, Japan), Bu_2SnL_2, Bu_2SnMHM_2, Bu_2SnDT_2, $(Bu_3Sn)_2O$ (ICN Pharmaceuticals, Inc., Life Sci. Group, Plainview, N. Y., USA). The purities of these compounds were higher than 95%. The stock solutions of tin compounds were prepared by dissolving them in 99.5%

ethanol (Wako Pure Chem., Osaka, Japan; Pesticide Analytical Grade). All reagents were analytical reagent grade. The cation-exchange resin for column chromatography (Amberlite CG-120, chromatographic grade, 200 mesh) was pre-washed in the usual manner, and conditioned with ethanol.[22]

Apparatus. Normal, reverse and differential pulse polarograms and cyclic voltammograms were measured on a Yanagimoto Voltammetric Analyzer (model P-1000) using a three-electrode cell. Throughout this study an aqueous saturated calomel electrode (SCE) and a spiral platinum electrode were used as a reference electrode and as a counter electrode, respectively. Cyclic voltammograms were measured with a hanging mercury drop electrode (HMDE) (Metrohm, Type EA290, electrode surface area 1.39±0.03 mm^2).

For DPASV, Yanagimoto Voltammetric Analyzer (P-1000) was used to supply both the applied potential for the pre-electrolysis and the voltage sweep for the stripping process. During pre-electrolysis the solution was constantly stirred by a Metrohm model E549 magnetic stirrer. The working electrode used was the same HMDE as that used in the measurement of cyclic voltammograms. The polarographic cell employed was Princeton Applied Research model K64.

The apparent pH values of ethanolic solutions were measured with a Hitachi pH meter molel F-7AD.

Procedure. Working solutions for all voltammetry were made up in constant ionic strength buffer medium (0.1 M in acetic acid and ammonia) at apparent pH 7.3. Unless otherwise stated, the solutions contained 50% ethanol and 0.002% Triton X-100.[5,9,11] Solutions were deoxygenated with a steam of purified nitrogen gas for 10 min prior to measurement, which was presaturated with ethanol–water (1:1) vapor.

For DPASV, after deaeration of the solution, a drop at the HMDE was formed and a constant voltage (−1.0 V for Bu_2SnX_2 and Ph_3SnCl, and −1.3 V for $(Bu_3Sn)_2O$) was applied for a given interval (60 s). The deposition proceeded in a stirred solution. After a quiescent period of 10 s, the electrode was polarized from the deposition potential to more positive values and the stripping peak was recorded. For every measurement the solution was deoxygenated for 2 min and a new drop was formed at the HMDE.

Results and Discussion

General Voltammetric Behavior. In order to develop a sensitive method for determining Bu_2SnX_2 (X=chloride, L, MHM, and DT), its voltammetric behavior, especially Bu_2SnCl_2, was investigated. Since Bu_2SnDT_2 is sparingly soluble in 50% (v/v) ethanol–water medium, it was not investigated.

Normal pulse polarograms (NPP) for Bu_2SnCl_2 in 50% (v/v) and 80% (v/v) ethanol–water media (apparent pH 7.3) are shown in Fig. 1. In both media, Bu_2SnCl_2 gives three reduction waves (I—III).[11] At 1×10^{-4} M (1 M=1 mol dm^{-3}) of Bu_2SnCl_2 in 50% ethanol, distortion is present at more negative potentials than −1.0 V (Fig. 1, curve 1), where the waves appear to split into several steps[9] which were ascertained from cyclic voltammetry. Compared with the respective potentials of three reduction waves of Bu_2SnX_2 (X=L and M) at −0.8, −1.0, and −1.4 V *vs.* SCE according to Scheme (1),[11] the first wave (I) in both media is probably attributed to a two-overlapped wave corresponding to the first and second steps, *i.e.* the formation of Bu_2Sn: which is polymerized to $(Bu_2Sn)_n$.[11] This is also confirmed by the fact that in tast polarography of Bu_2SnCl_2 the limiting current of the first wave (I) in 50% ethanol is the same as that in 80% ethanol. Further, the second wave (II) is probably due to a two-electron reduction of Bu_2Sn: to the hydride Bu_2SnH_2 (third step in Scheme 1).

There is significant adsorption of both Bu_2SnX_2 (X=chloride, L, and MHM) and their reduction products in 50% ethanol, as demonstrated by the appearance of a maximum at the first wave in normal[15] and reverse pulse polarograms, and the depression of electrocapillary curves of Bu_2SnX_2 at both sides of the maximum (Fig. 1). On the other hand, the first wave is accompanied with no maximum in 80% ethanol, indicating that there is no adsorption of the depolarizers and their reduction products in 80% ethanol, as was observed by Fleet and

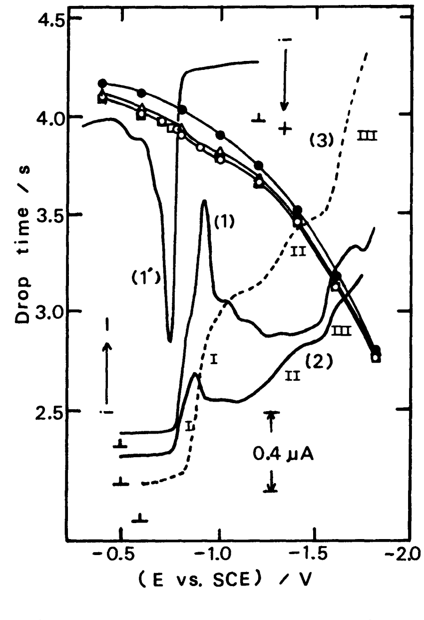


Fig. 1. Normal pulse and reverse pulse polarograms (NPP and RPP) of Bu_2SnCl_2 and electrocapillary curves (ECC) of Bu_2SnX_2 in the 0.1 M acetic acid–0.1 M ammonia buffer solution (pH 7.3) containing 0.002% Triton X-100.
Conditions of NPP and RPP: Ethanol, (1)(1′)(2) 50% (v/v) and (3) 80% (v/v); $[Bu_2SnCl_2]$=(1)(1′)(3) 1×10^{-4} M, (2) 4×10^{-5} M; (Initial potential *vs.* SCE) /V=(1)(2) −0.5, (1′) −1.2, (3) −0.6. Conditions of ECC: Ethanol, 50% (v/v); $[Bu_2SnX_2]$=-●- 0 M, -○- 1×10^{-4} M Bu_2SnCl_2, -□- 1×10^{-4} M Bu_2SnL_2, -△- 1×10^{-4} M Bu_2SnMHM_2.

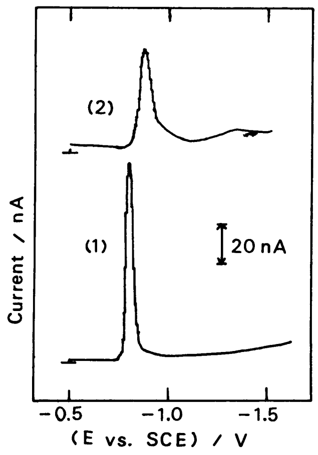


Fig. 2. Differential pulse polarograms (DPP) of 1×10^{-4} M Bu_2SnCl_2 solutions in 50% (v/v) and 80% (v/v) ethanol. Ethanol, (1) 50% (v/v) and (2) 80% (v/v), Conditions: modulation amplitude, 5 mV; pulse repetition time, 1 s; scan rate, 5 mV s^{-1}.

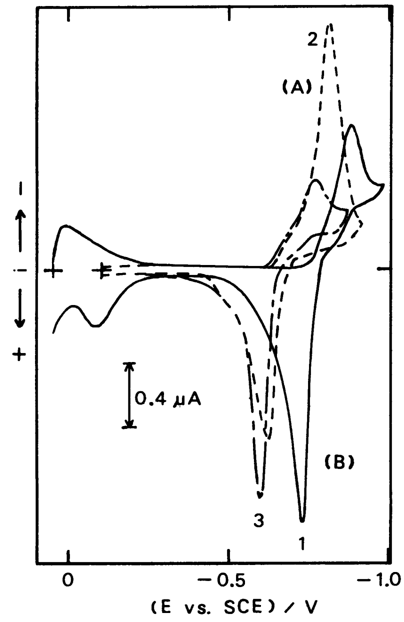


Fig. 3. Cyclic voltammograms of Bu_2SnX_2 in 50% (v/v) ethanol-water medium. (1) 1×10^{-4} M Bu_2SnCl_2, (2) 7×10^{-5} M Bu_2SnL_2, (3) 1×10^{-4} M Bu_2SnMHM_2; Starting potential, (1) +0.05 V, (2)(3) −0.1 V; scan rate, 200 mV s^{-1}.

Fouzder.[11)]

Differential pulse polarograms (DPP) of Bu_2SnCl_2 show one distinct peak in both 80 and 50% ethanol-water media as shown in Fig. 2. A similar DPP was obtained for Bu_2SnL_2 in 50% ethanol. The peak in 50% ethanol (curve 1) is narrower and higher than that in 80% ethanol (curve 2) at the same concentration (1×10^{-4} M) of Bu_2SnCl_2. The half-widths ($W_{1/2}$) of Bu_2SnCl_2 in 50 and 80% ethanol and Bu_2SnL_2[11)] in 80% ethanol without surface-active agents at the modulation amplitude (ΔE) of 50 mV are 57, 88, and 90 mV, respectively. The smaller $W_{1/2}$ in 50% ethanol than those in 80% ethanol probably depends partially on the adsorption of the depolarizer and its reduction product(s) in 50% ethanol.

Table 1. Peak potentials of dibutyltin compounds for cyclic voltammograms

Compounds (Bu_2SnX_2)	$E_{p,c}$[a)] (V)	$E_{p,a}$[b)] (V)
Bu_2SnCl_2	−0.90	−0.72
Bu_2SnL_2	−0.83	−0.65
Bu_2SnMHM_2	−0.77	−0.60

Conditions of cyclic voltammograms are the same as those in Fig. 3.

a) Peak potential of the cathodic peak. b) Peak potential of the anodic peak.

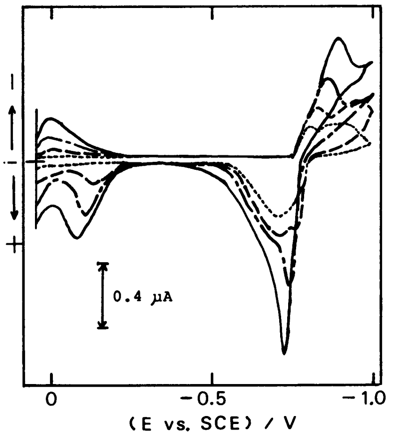


Fig. 4. Effect of scan rate on cyclic voltammograms of Bu_2SnCl_2. $[Bu_2SnCl_2]=1\times10^{-4}$ M; scan rate/mV s^{-1}= ---- 20, — — 50, —-— 100, —— 200.

Cyclic voltammograms of Bu_2SnX_2 (X=chloride, L, and MHM) in 50% ethanol are shown in Fig. 3, and the peak potentials on the forward and reverse scans are also shown in Table 1. Peaks (A) for Bu_2SnX_2 occur on the forward or cathodic scan corresponding to the reduction of Bu_2SnX_2. Peaks (B) for Bu_2SnX_2 on the reverse or anodic scan are observed corresponding to the re-oxidation or "stripping" of the products of (A) from the electrode.[16)] This finding suggests that the reduction products of Bu_2SnX_2 accumulated on the electrode are readily re-oxidized. The current-voltage curve for the re-oxidation or "stripping" can be utilized for the determination of traces of Bu_2SnX_2 by ASV.

In cyclic voltammetry, scan rate is probably most important experimental parameter for studying the adsorption of reactants or products at the electrode.[17)] The dependence of the scan rate on the cyclic voltammetric curve for 1×10^{-4} M Bu_2SnCl_2 in 50%

ethanol is shown in Fig. 4. At the relatively lower scan rate, two cathodic and two corresponding anodic peaks were observed, one of the latter being a shoulder. As the scan rate increases, the respective cathodic and anodic peak currents increase. With further increase of the scan rate above 100 mV s^{-1}, the cathodic and anodic peaks are reduced to one peak, and respective peak currents increase. This cyclic voltammetric behavior described above is analogous to the case, where the reduction product is strongly adsorbed on the stationary electrode,[17] as demonstrated by pulse polarography and electrocapillary curves.

Fleet and Fouzder[11] stated that in Scheme (1) $Bu_2Sn^{\dagger}$ ion radical is stable in 80% (v/v) ethanol, but is unstable in <50% (v/v) ethanol as is shown by disappearance of the second wave in 50% ethanol. However, various electrochemical behavior of Bu_2SnX_2 as described above probably indicates that the first and second steps in Scheme (1) proceed at the very close potentials in 50% ethanol, and the reduction products are significantly adsorbed at the mercury electrode. The cause of this difference between both studies is not clear, but is presumably due to the presence or absence of Triton X-100 in ethanolic solutions.

DPASV. Since the voltammetric studies described above suggest the possibility of determining Bu_2SnX_2 by ASV in 50% ethanol, the detailed DPASV behavior of Bu_2SnX_2 (X=chloride, L, MHM, and DT), especially that of Bu_2SnCl_2, was investigated in 50% ethanol in order to develop a more sensitive method, and the DPASV behavior of Bu_2SnX_2 was partly compared to those of tributyltin compounds and Ph_3SnCl.

Typical differential pulse anodic stripping voltammograms for Bu_2SnCl_2, $(Bu_3Sn)_2O$, and Ph_3SnCl obtained in 50% ethanol are shown in Fig. 5. Similar voltammograms were obtained for the other Bu_2SnX_2 in question. The half-widths for the stripping peaks of Bu_2SnCl_2, $(Bu_3Sn)_2O$, and Ph_3SnCl are 30, 107 and 95 mV, respectively.

The variation of the stripping peak current with the mass concentration of Bu_2SnCl_2 was examined. The peak current rises linearly with the concentration of Bu_2SnCl_2 in the range of 3 to 50 ppb (1 ppb=1 μg dm^{-3}) at the deposition time of 60 s. It is to be stressed here that this linear range is a function

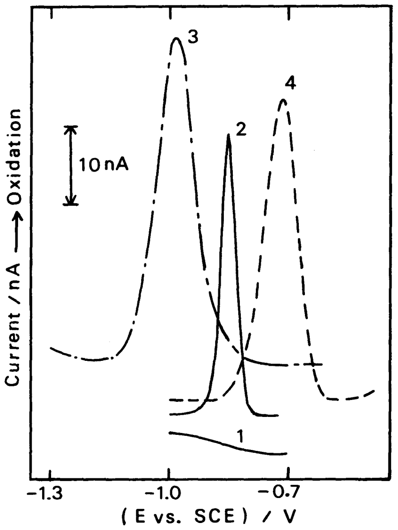


Fig. 5. Typical differential pulse anodic stripping voltammograms of Bu_2SnCl_2, Ph_3SnCl, and $(Bu_3Sn)_2O$ in 50% (v/v) ethanol–water medium of the same composition as in Fig. 1. Pulse repetition time, 0.1 s; modulation amplitude, 50 mV; scan rate 20 mV s^{-1}; deposition potential, (1) −1.0 V, (2) −1.0 V, (3) −1.3 V, and (4) −1.0 V; deposition time, 60 s (stirred); equilibration period, 10 s (unstirred). $[Bu_2SnCl_2]$/ppb=(1) 0 (blank), (2) 24.9; $[(Bu_3Sn)_2O]$/ppb=(3) 129; $[Ph_3SnCl]$/ppb=(4) 115.

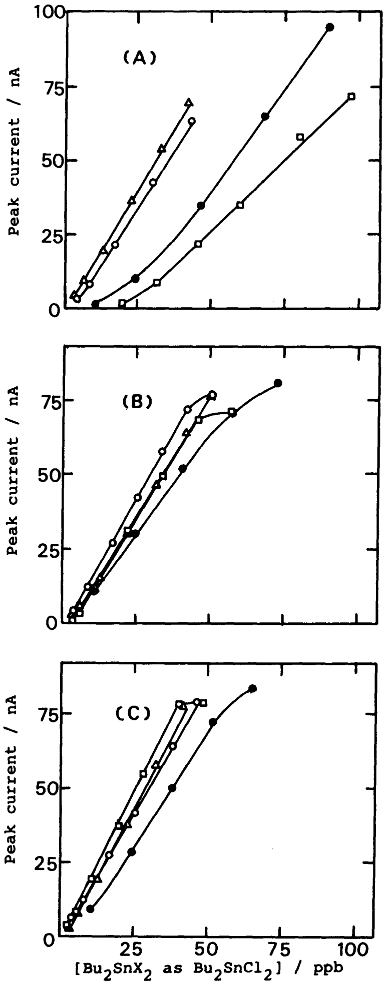


Fig. 6. Effect of potassium chloride on calibration curves of Bu_2SnX_2 in 50% (v/v) ethanol–water medium. [KCl]/M=(A) 0, (B) 0.1, and (C) 0.5, Species of Bu_2SnX_2; -○- Bu_2SnCl_2, -△- Bu_2SnDT_2, -●- Bu_2SnMHM_2, -□- Bu_2SnL_2.

of deposition time, stirring rate, *etc.*, and is not always valid under various conditions. Further, the rise is smaller than the linear value up to 70 ppb and the decrease occurs gradually again. This behavior is expected when a film of insulating material is formed as the reduction product.[9] Beyond a certain critical concentration, at which point the electrode is completely covered with the film, the stripping peak current increases slowly, if at all, with increasing depolarizer concentration. These findings indicate that, in the DPASV steps, the reduction of Bu_2SnCl_2 and the re-oxidation of its reduction product(s), which is only stabilized by the adsorption onto the mercury electrode,[9,11] should occur on the electrode surface.

The lower limits of detection of Bu_2SnCl_2, $(Bu_3Sn)_2O$, and Ph_3SnCl are 3, 2.5, and 7 ppb, respectively. The relative standard deviation at 8.4 ppb of Bu_2SnCl_2 (eight runs) was 3.1%.

The comparison of calibration curves of the respective Bu_2SnX_2 is of interest in connection with its chemical property. Each Bu_2SnX_2 in 50% ethanol–water medium gives a different calibration curve and further each calibration curve varies with the concentration of potassium chloride added in 50% ethanol–water medium (Fig. 6), where all concentrations of Bu_2SnX_2 are represented as that of Bu_2SnCl_2. Without potassium chloride (Fig. 6 A), the slopes of calibration curves giving straight lines increase in the following order: $Bu_2SnL_2 < Bu_2SnMHM_2 < Bu_2SnCl_2$—$Bu_2SnDT_2$. Moreover, the intercepts at zero peak current of these straight lines decrease in the above order. These findings indicate that the DPASV steps of Bu_2SnX_2 occur readily in the above order. With increasing concentration of potassium chloride, the calibration curves of Bu_2SnL_2 and Bu_2SnMHM_2 approach gradually to that of Bu_2SnCl_2, but the calibration curve of Bu_2SnMHM_2 does not overlap even at 0.5 M potassium chloride. It was also observed that the stripping peak potential (E_p) of Bu_2SnMHM_2 is more positive than those of others in a medium without potassium chloride, and E_p of Bu_2SnMHM_2 approaches to those of others with increasing concentration of potassium chloride. These facts indicate that L and MHM of Bu_2SnX_2 are gradually replaced by chloride, and the replacement of MHM by chloride is not so easy as L. Further, the different DPASV behavior of Bu_2SnMHM_2 from others is probably ascribed to the effect of an olefinic double bond of Bu_2SnMHM_2.[11] On the other hand, the fact that the calibration curve of Bu_2SnDT_2 is very close to that of Bu_2SnCl_2 even in a medium without potassium chloride is presumably attributed to a strong and stable adsorption of Bu_2SnDT_2 and its reduction product(s) at the HMDE. This may be the result of the interaction between mercury and sulfur, as was observed for dioctyltin bis(mercaptoacetate) in 80% ethanol.[12] From the results described above, the bond between tin atom and X in Bu_2SnX_2 seems to possess a covalent property enhancing in the reverse order as mentioned above.

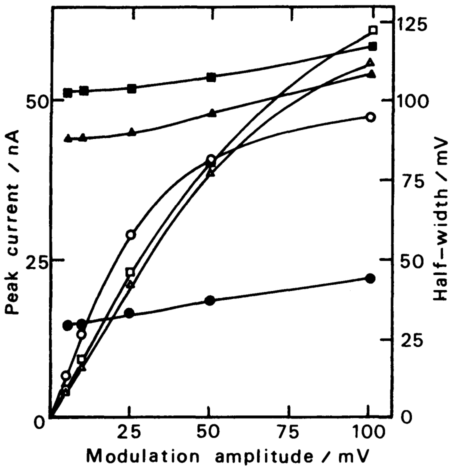


Fig. 7. Effects of modulation amplitude on peak current and half-width. -○-, -●- $[Bu_2SnCl_2]=25.2$ ppb; -△-, -▲- $[Ph_3SnCl]=115$ ppb; -□-, -■- $[(Bu_3Sn)_2O]=129$ ppb. Peak current, -○-, -△-, -□-; half-width, -●-, -▲-, -■-.

Optimization of Instrumental Parameters: The effects of various instrumental parameters on the stripping peak current are shown below.

The effects of the ΔE on the peak current and the $W_{1/2}$ for Bu_2SnCl_2, $(Bu_3Sn)_2O$, and Ph_3SnCl are shown in Fig. 7. The peak currents of these compounds are proportional to the ΔE up to 25 mV. The $W_{1/2}$ for these compounds also increase with an increase in ΔE. These findings are generally observed in DPASV.[18–20] On the grounds of sensitivity and selectivity the modulation amplitude of 50 mV was chosen for this study.

The peak current is proportional to the deposition time up to 2 min. Hence, the deposition time of 1 min was chosen throughout this study.

The effect of the scan rate on the peak current of Bu_2SnCl_2 was examined over the scan rate of 5 to 100 mV s^{-1}. The peak current increased steeply with increasing scan rate in the range of 5—20 mV s^{-1} and increased gradually above 20 mV s^{-1}.

The plots of the deposition potential (E_{dep}) *vs.* peak current for Bu_2SnCl_2, $(Bu_3Sn)_2O$, and Ph_3SnCl are shown in Fig. 8. The plots for the other Bu_2SnX_2 were similar to that of Bu_2SnCl_2. The maximum peak current for each compound was observed in the narrow range. When deposited at −1.0 V, Bu_2SnCl_2 is co-deposited considerably with Ph_3SnCl, but scarcely with $(Bu_3Sn)_2O$.

Several DPASV behavior of Bu_3SnCl was also investigated and the DPASV behavior obtained for Bu_3SnCl was the same as that of $(Bu_3Sn)_2O$ described above.

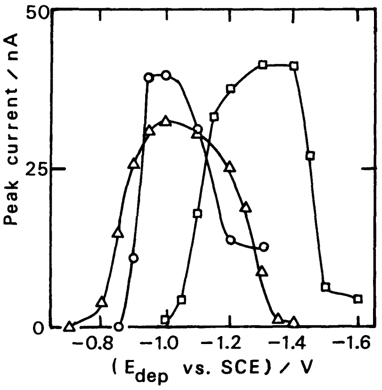


Fig. 8. Effect of deposition potential on peak current. -○- [Bu_2SnCl_2] = 25.2 ppb; -△- [Ph_3SnCl] = 100 ppb; -□- [$(Bu_3Sn)_2O$] = 129 ppb.

On the grounds of the results described above, the instrumental parameters were chosen for the conditions shown in Fig. 5.

Stability of Stripping Peak Current of Bu_2SnX_2: Fleet and Fouzder[11] claimed that $Bu_2Sn^{\dagger}$ ion radical is unstable in <50% (v/v) ethanol as described above. However, each stripping peak current of Bu_2SnX_2 in 50% ethanol was constant over the standing time at least up to 180 min under the stream of nitrogen gas.

Effect of Coexisting Substances: As can be seen in Fig. 6, the peak current of Bu_2SnCl_2 increased slightly with increasing concentration of potassium chloride added in 50% ethanol–water medium.

The effects of Ph_3SnCl and Bu_3SnCl on the determination of Bu_2SnCl_2 was also examined. As described above, Bu_2SnCl_2 is co-deposited with Ph_3SnCl, but scarcely with Bu_3SnCl when deposited at −1.0 V (Fig. 8). The presence of Ph_3SnCl in the concentration above 4 ppb depressed the peak current of Bu_2SnCl_2 (25.2 ppb). The presence of Bu_3SnCl at *ca.* 30 ppb scarcely affected the peak current of Bu_2SnCl_2 (25.2 ppb).

Determination of Bu_2SnX_2. On the basis of the above detailed study, an analytical method for the determination of Bu_2SnX_2 in natural water was developed. The proposed method involves extraction[21] and cleaning up by chromatography on a cation-exchange resin[22] in order to avoid interferences from heavy metals and organic materials in the measurement of DPASV.

To 250 ml of natural water was added 10 grams of sodium chloride (except for sea water) and 2 ml of hydrochloric acid (36%), and then Bu_2SnX_2 was extracted twice with 25 ml of 50% ethyl acetate–hexane. The extract was dried over anhydrous sodium sulfate, concentrated to about 5 ml by use of Kuderna-Danish concentrator and then evaporated to near dryness under the stream of nitrogen gas. The concentrate was dissolved in 10 ml of ethanol. The ethanolic solution was passed through a cation-exchange resin column (2×5 cm). After washing the column with 20 ml of ethanol and 10 ml of 5% (v/v) water–ethanol, Bu_2SnCl_2 was eluted with 13 ml of 5% (v/v) hydrochloric acid–ethanol. During extraction and cleaning up by chromatography, Bu_2SnX_2 will be converted to Bu_2SnCl_2. The eluate was neutralized to approximately pH 7.0 with ammonia and acetic acid. After adding buffer (pH 7.0) and Triton X-100 the solution was diluted to 25 ml with water, whereupon the final concentration of ethanol became 50% (v/v). Then, Bu_2SnCl_2 was determined by DPASV by use of the standard addition method.

Recovery tests of Bu_2SnCl_2 (1 μg) from river water and sea water were carried out, and the recovery percentages were 67 and 91%, respectively. The lower recovery percentage from river water is probably ascribed to the lower extractability of Bu_2SnCl_2 due to the absence of ions such as bromide.[23]

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