

Study on Electrochemical Properties of TBT(Tributyltin)

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The chemical behavior and properties of the redox state of environmental pollutants was investigated using electrochemical methods. The purpose was to measure the variations in the redox reaction of differential pulse polarograms and cyclic voltammograms. The results observed the influences on redox potential and current of various factors including concentration, temperature, salt, and pH. These were established factors as the effect of the redox reaction. It can be clearly recognized that the electrode reaction are from reversible to irreversible processes. Also, it was mixing with reaction current controlled.

Key words : differential pulse polarography, cyclic voltammetry, charge transfer, reversible, potential, reaction control, cathodic, anodic, diffusion control

1. Introduction

Most previous toxicology and epidemiology studies on environmental contaminants have focused on single substances that enter the body by a particular means, e.g. breathing, ingestion, or absorption through the skin. However, in the real world, people are exposed to a myriad of chemicals that can enter the body through more than one pathway. Consequently, the relationship between environmental concentrations of pollutants and the amounts that end up in humans is still unknown. The US Environmental Protection Agency(US EPA) is attempting to gather information on human exposure through a variety of pathways to certain classes of chemicals, such as pesticides and metals. In effect, how many environmental contaminants actually end up in human bodies. In addition, the US EPA wants to use the data to determine how people are actually exposed to pollutants, e.g. through their diets or drinking water, the air they breathe, or skin contact and which activities bring them into contact with pollutants. This US EPA project on multipathway, multichemical exposure is called the National Human Exposure Assessment Survey(NHEXAS). Conceptualized in 1991, NHEXAS consists of three pilot studies on the exposure of hundreds of U.S.

residents to metals, pesticides, and volatile organic compounds. Two of the studies also included polycyclic aromatic hydrocarbons. The chemicals investigated in the study were selected because they are either known to pose or are strongly suspected of posing health risks, are found in at least two environmental media(air, water, or soil), and are of concern to the US EPA. NHEXAS expands on and replaced the US EPA's national human adipose tissue survey, which ended in 1992. That survey involved the monitoring of human fat tissue for approximately 130 persistent organochlorine pesticides and polychlorinated biphenyls. Another part of NHEXAS involved determining relationships between activities reported by the participants and measurements of environmental concentrations, exposure, and biomarkers. In a 1999 review of the preliminary data from the pilot studies, EPA's Science Advisory Board(SAB) said : "when completed, NHEXAS should provide a greatly improved understanding of human exposure to selected pollutants. This, in turn, will be helpful in determining the most effective strategies to reduce the public's risk to hazardous environmental chemicals." The same SAB review pronounced NHEXAS to be "an excellent project that has significant promise for improving public health in a cost effective manner." Graham commented that

NHEXAS will upgrade the scientific understanding of human exposure to pollutants¹). The Kyung-hyang Shinmun also reported on similar statistical data (from 4. 1999 to 8. 2000) from a research institute in Korea. However, the newspaper article expressed concern about the limited resources that had been allocated to analyze the data. Researchers investigated the areas of Sum Jin river (Hadong in Kyung Nam) and Eui Am lake (Chum-Cheun in Kang Won). The data included the levels of the target chemicals in the air, food, drinking water, soil, and dust around the houses. The exposure of the local residents to metals, pesticides, and volatile organic compounds was also measured. As a result, the investigation identified 130 environmental contaminants in the air, soil, river, and lake²).

The survey involved the monitoring of about 130 persistent organochlorine pesticides, polychlorinated biphenyls, dioxine, bis-phenol A³, di(2-ethylhexyl)pth-alate, tributyltin, polybiphenylchloride, and hexachlorobenzene etc. Accordingly, the current study investigated the detailed influence of various conditions on certain contaminating materials (tributyltin).

2. Experimental Procedure

2.1. Materials and Instrumentation

All reagents and solvents were purified according to conventional procedures. Reagent grade tributyltin (99.0 % purity : Aldrich Co) was used without any further purification and kept in a glovebox under an argon atmosphere prior to use. All reagents were high purity grade. Tetraethylammonium perchlorate (TEAP : Aldrich) was dried at 80 °C under a vacuum for 3 days and used as a supporting electrolyte. The experimental solution was deoxygenated by purging for at least 15 min with pre-purified nitrogen gas.

The cyclic voltammograms were recorded using a PARC Model-303A static mercury dropping electrode (SMDE) and PARC 264A polarographic analyzer equipped with a PARC Model KE-0089 XY recorder. A three-electrode cell consisting of a working electrode, platinum-wire counter electrode, and silver/silver chloride reference electrode was used. The reference electrode was kept in a compartment containing the appropriate supporting electrolyte (TEAP) and a freshly dropped mercury and platinum wire as the counter electrode.

Table 1. Comparison of parameters with differential pulse polarography and cyclic voltammetry methods

Complex	Redox steps	Differential pulse polarography				Cyclic voltammetry				
		$E_{1/2}$	E_{Pc}	$(E_{Pc})_2 - (E_{1/2})_1$	$\Delta E_p (E_{Pc})_2 - (E_{Pc})_1$	$E_{1/2}$	E_{Pc}	E_{Pa}	$(E_{Pc})_2 - (E_{1/2})_1$	$\Delta E_p (E_{Pc})_2 - (E_{Pc})_1$
[TBT]	1st wave	-1.01	-1.10			-1.03	-1.12	-1.00		0.12
				0.83	0.74	-1.30			0.83	1.30
	2nd wave	-1.78	-1.84			-1.77	-1.86	0.00		1.85

$\Delta E = E_p^2 - (E_{1/2})^1$ (differential-pulse-half-wave potential ; 1(first), 2(second)), $\Delta E_p (E_{Pc} - E_{Pa})$ (cyclic voltammetry ; peak to peak separation), ΔE_p (differential pulse method ; $E_p^2 - E_p^1$), $E_{p/2}$ (half peak potential) ; ($| E_{Pc} - E_{p/2} |$ width of wave), E_{Pc} : cathodic peak potential, E_{Pa} : anodic peak potential.

Table 2. Cyclic voltammetry characterization of the TBT in acetonitrile with 0.1 M TEAP (scan rate : 100 mV/s) (25 °C)

Complex	Redox Steps	$E_{1/2}$	E_{Pc}	E_{Pa}	ΔE_p	iP_c	iP_a	iP_a/iP_c	n	Λ_M	K_c
		(V)			(μA)						
[TBT]	1st wave	-1.03	-1.12	-1.00	0.12	0.97	1.00	1.03	1.00	0.47	1.03
	2nd wave	-1.77	-1.86	0.00	1.85	0.25	0.00	0.00			

iP_c : cathodic peak current ; iP_a : anodic peak current ; n : electron number of redox reaction ; Λ_M : molar conductance ; K_c : comproportionation constant.

3. Results and Discussion

3.1. Electrochemical Methods and Measurements

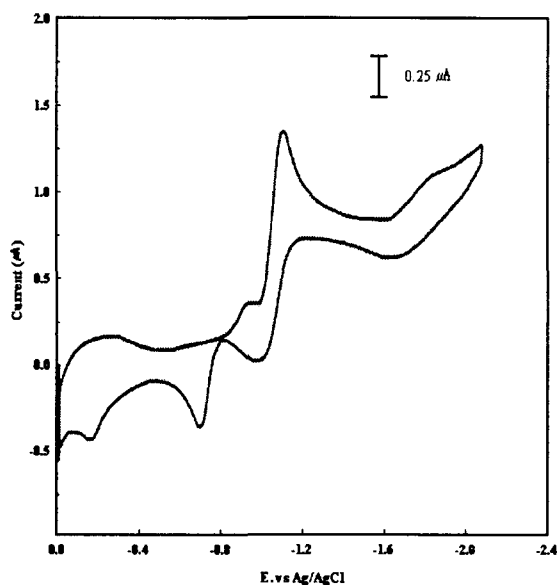


Fig. 1. Current-potential curve for differential pulse polarography of 1mM TBT(scan rate : 200 mV/s).

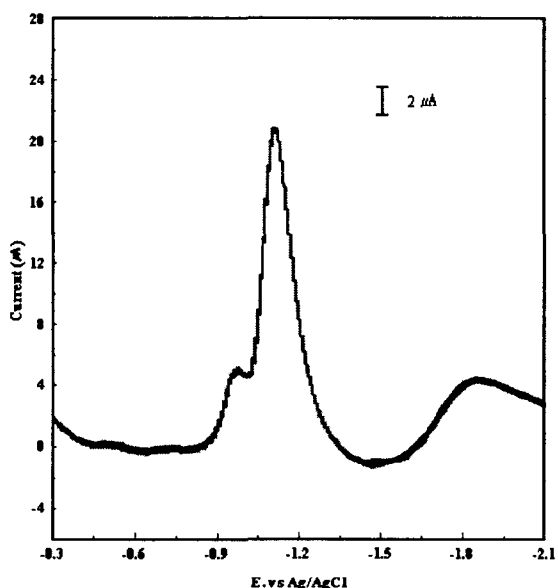


Fig. 2. Cyclic voltammogram for 1mM TBT in acetonitrile with 0.01M TEAP at 25 °C(scan rate : 200 mV/s).

Differential pulse polarographics(DPP) and cyclic voltammograms(CV) of the tributyltin were recorded in an acetonitrile solution under a nitrogen atmosphere with 0.1M TEAP. The results are shown in Figs. 1 ~ 5 and Tables 1 and 2. The curves of the peak to peak separation in the DPP and CV methods are presented as a two-step electrochemical charge transfer. The $\text{Tin}(\text{II})$ compound exhibited a one-step reduction and three-step oxidation. Evidence of a one-electron charge from the redox processes was obtained when $n = 1.03$ using coulometrics. Here, the techniques of differential pulse polarography and cyclic voltammetry were applied to determine the response using the experimental data. As shown Figs. 1 and 2 and Table 1, the E_s and E_p values obtained from the DPP and CV methods did not match for all the steps, yet the $(E_{pc})_2 - (E_t)_1 = 0.83$ V values obtained by the two methods were clearly in good agreement. However, when comparing the E_{pc} values, the potential values from the CV method indicated a more negative potential($E_{pc1} = -1.12$ V ; $E_{pc2} = -1.86$ V) than values($E_{pc1} = -1.10$ V ; $E_{pc2} = -1.84$ V) obtained using the DPP method. Accordingly, it would appear that the potential efficient was due more to the wave width than the pulse amplitudes. Although cyclic voltammetry instruments apply both cathodic and anodic potentials, the differential pulse polarographic is only relative the cathodic potential. In this case, the E_{pa} value should not be compared with the DPP method. Consequently, the CV method is applied more widely than the DPP method. More important, the $(E_{s1})_1$ and $(E_{s2})_2$ values obtained by the DPP and CV methods were almost in good agreement ($\Delta E_{s1} = 0.02$ V and $\Delta E_{s2} = 0.01$ V).

In general, a good agreement was found with $\Delta E_s = \pm 20$ mV(0.02 V), as determined by the width of the cyclic voltammetric method. In contrast, the ΔE_p value obtained by the DPP method was 0.74 V, whereas that obtained from the CV method was 0.12 V(1st wave) and 1.85 V(2nd wave). This was also observed for all the CV measurement values. However, the most positive potential exhibited by the 1st wave and 2nd wave was not an oxidation reaction. It would appear that only one wave for which it was not experimentally possible to detect a 2nd anodic wave. In all cases, these results of the ΔE_p values were chemically irreversible. As

shown in Table 1, cathodic peak potential(E_{pc}) values obtained from DPP and CV methods were perfectly coincidence to the two steps. We would estimated that these potentials was because of the accuracy of the measured width in the two methods. Fig. 2 and Table 2 summarizes the main cyclic voltammetry characteristics of TBT, at a scan rate of 200 mV/s. we focused first on the variation of E_4 values, which were taken as the average between the cathodic and anodic peak potentials. Half wave potentials of the two waves appears at $E_4 = -1.03$ V of a 1st wave and a $E_4 = -1.77$ V of a 2nd wave. Fig. 3 obtained from Fig. 2 presents the variation in the half wave potential(E_4) derived from the votammetric curves relative to temperatures. Considering at 25 °C, the half wave potentials(E_4) was maintained as an cathodic potentials at 15, 35, 45, and 55 °C, respectively, it indicated the reduction. On the other hand, the potentials(E_4) efficient of redox reaction were observed when the 1st and 2nd waves appears a single and couple waves at 25 °C. This occurred simultaneously with only reduction and oxidation reaction at 25 °C. Here, more important was exhibited only reduction waves when it would be higher than at 25 °C. Here, from the experimentally related to the temperatures, it was not 1st wave but 2nd wave occurred distinctly break down of wave. As shown by the appearance of the 2nd wave in the Fig. 3, evidence of reductive and oxidative decomposition was holding the potentials more than at 25 °C. In the region of real concern experimental(i vs. E), where the wave is distorted or disappeared a measurement of the current and potentials is impossible. Experimentally, such an arrangement may not be possible due to impurities, solvent break down, counter ion interference, or other problems. Table 2 summarizes the main cyclic voltammetry characteristics of the TBT, at a scan rate of 200 mV/s. we focused first on the variation of E_4 values, which were taken as the average between the cathodic and anodic peak potentials. Half wave potentials of the two waves appears at $E_4 = -1.03$ V of a 1st wave and a $E_4 = -1.77$ V of a 2nd wave. Fig. 2 shows a reduction 1st wave at $E_{pc} = -1.12$ V and an oxidation wave at $E_{pa} = +1.00$ V, a reduction 2nd wave at $E_{pc} = -1.86$ V and an oxidation wave at $E_{pa} = 0.00$ V. As indicated by the data in Table 2, all of the 1st

and 2nd waves were irreversible since the peak potential difference(ΔE_p) was larger than 60 mV. Their anodic(a) and cathodic(c) peak current⁴ ratios of the 1st and 2nd wave were $iP_{a1}/iP_{c1} = 1.03$ and $iP_{a2}/iP_{c2} = 0.00$, at a sweep rate of 200 mV/s.

The value of the 1st wave is significantly more 1.03 than the corresponding 1.0 and the 2nd wave is the zero. In this case, these processes are not agree with respect indicating a significant degree of the these values. In contrast, from the 2nd wave, anodic peak current appears not. These assignments are based on the fact that it showed the irreversible nature of the one electron reduction process. one electron charge transfer from the redox processes was obtained by coulometric with $n = 1.02$ value. Molar conductivity(\wedge_M) was indicated 0.47, this compound behaviors as nonelectrolyte in acetonitrile solvent with molar conductivities corresponding to the lowest value proposed by Geary⁵. The relation of the concentration at equilibrium is expressed by the compropotion cation constant, K_c .

$$K_c = \exp\left[\frac{(E_{1/2}^0)_1 - (E_{1/2}^0)_2}{RT} n_1 n_2 F\right]$$

where $n_1 = n_2 = 1$ (electron number), $K_c = \exp(\Delta E_4 / 25.69)$ at 298 K, with that method, value of $K_c = 1.03$ is obtainable in the range $-1.03 \text{ V} < \Delta E_4 < -1.77 \text{ V}$. This value is a sufficiently small compropotionation constant(K_c). Myer and Shain⁶ have given a curve applicable in the range for the width of a multistep response, ($E_{pc} - E_{p/2}$) vs. ΔE_4 . For $n_1 = n_2 = 1$, this would appear to limit their method to $K_c \leq 7$. However, we will show that their method can be extended to any value of ΔE_4 . On the other hand, we can be applied over the whole experimentally accessible range of ΔE_4 values⁷. As mentioned above, the relative more important of the experimental value, $K_c = 1.03$ is clearly illustrated in a comparison of the Myer and Shain method($K_c \leq 7$). This value is quit analogue to $K_c \leq 7$ value. With the methods of differential pulse voltammetry and cyclic voltammetry, the values of K_c for the compropotionation constant are about the same in the two cases. Table 2 show that K_c calculated to 0.02 V(20 mV) from DPP method and 0.01 V(10 mV) from CV method. Our experimental result(Table 2) indicate the width method of DPP and CV give ΔE_4 values that agree within about ± 3 mV. In the region of special

3.3. Influence of Temperature for Added Salt

Organo-tin compounds undergo abigenetic and biotic degradation processes in natural condition. But butyltin compounds may persist for several years in anoxia condition (WHO, 1980). Organo-tin particular tributyltin (TBT) are considered to be chemicals dangerous because of their deleterious effects on non-target marine organisms.

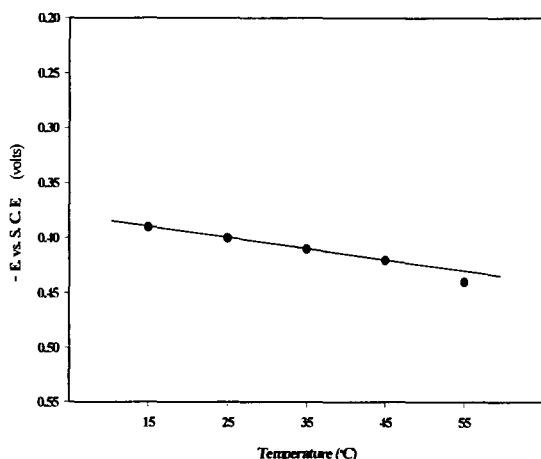


Fig. 4. Plot of $E_{1/2}$ vs. temperature for redox reaction with TBT in 0.35 % sodium chloride (salt).

As shown in Fig. 4, cyclic voltammogram of TBT in 0.35 % NaCl solution appears to a single reduction wave. Fig. 4 is plotted of half wave potentials ($E_{1/2}$) versus temperatures. This single wave was maintained by the cathodic potential at all temperatures. These results revealed more negative potentials the gradually increasing at temperatures. Thus, hydrogen with CH bond in tributyltine ($\text{CH}_3(\text{CH}_2)_3\text{SnCH}=\text{CH}_2$) was expected to be displaced by Cl^- ion NaCl. We believe that the negative potential consumed hydrogen ions. Accordingly, the reduction potential of the temperature in 0.35 % NaCl solution is speculated that it is increased the gradual with temperature increasing. We conclude that the product of nonelectroactive and either impedes the reduction of hydrogen ions in salt solution or exposed to a depleted of reactants in the diffusion layer adjacent to the electrode. Accordingly, TBT is not easily to be degradation in water or seawater (0.35 % NaCl). From these results, we was known that TBT exhibited slowly oxidation. But it was fast

than in water.

3.4. Influence of pH on Redox Reaction

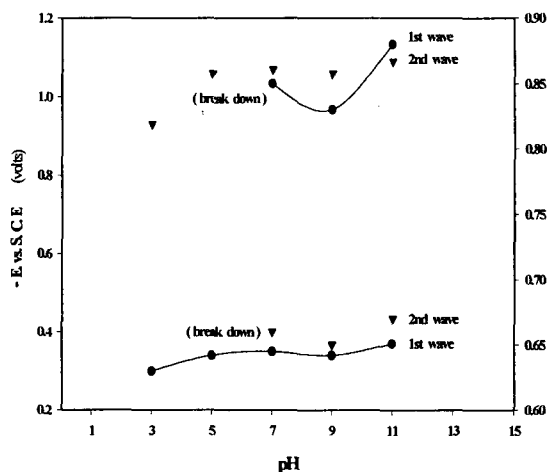
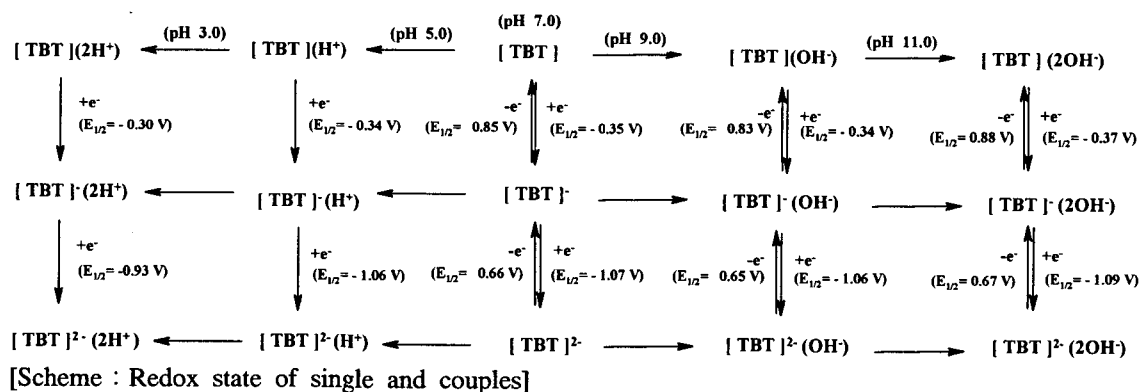


Fig. 5. Plot of $E_{1/2}$ vs. pH for redox reaction with tributyltin at 25 °C (● : reduction potential ; ▼ : oxidation potential).

From Fig. 5 and Table 3, the potential efficiency of the 1st and 2nd curves relative to pH was maintained as a cathodic and anodic potential on various pH. The TBT exhibited a cathodic reduction potential in the 1st and 2nd wave at all pH, but its showed cathodic and anodic potential more than at pH 5.0. Reduction and oxidation potential shifted with the 1st and 2nd curves as follows : pH 3.0 ($(E_{1/2})_1 = -0.30$ V, $(E_{1/2})_2 = -0.93$ V) ; pH 5.0 ($(E_{1/2})_1 = -0.34$ V, $(E_{1/2})_2 = -1.06$ V) ; pH 7.0 ($(E_{1/2})_1^c = -0.35$ V, $(E_{1/2})_1^a = 0.85$ V, $(E_{1/2})_2^c = -1.07$ V, $(E_{1/2})_2^a = 0.66$ V) ; pH 9.0 ($(E_{1/2})_1^c = -0.34$ V, $(E_{1/2})_1^a = 0.83$ V, $(E_{1/2})_2^c = -1.06$ V, $(E_{1/2})_2^a = 0.65$ V) ; pH 11.0 ($(E_{1/2})_1^c = -0.37$ V, $(E_{1/2})_1^a = 0.88$ V, $(E_{1/2})_2^c = -1.09$ V, $(E_{1/2})_2^a = 0.67$ V) (where, c : cathodic ; a : anodic ; 1, 2 : waves). More important fact arise break down of oxidation at pH 3.0 and 5.0, but occurred with rapidly reduction. At this point, it showed clearly of oxidative decomposition when the observed potential is given by the holding of potential ($E_{1/2}$) responses. The redox reaction of compound was obtained to couple of the 1st and 2nd wave to at pH 7.0 till 11.0. The redox potential values of the 1st and 2nd waves at pH 7.0 were obtained more an absolute value than at pH 3.0 and 5.0. Again, to at pH 9.0 was obtained less than at pH 7.0. On the other hand, at pH 11.0 was obtained



the most an absolute value. And these two waves were diminished above at pH 11.0. Therefore, the compound would be break down above at pH 11.0. Such a phenomenon which occurs in acetonitrile was believed using as solvent or decomposition. The redox processes of pH was shown as follow.

4. Conclusions

The compound exhibited only redox couples(1st and 2nd steps) and single(3rd step) reaction at 25 °C. However, its appears only reduction waves at all temperatures with except for at 25 °C. The 1st and 2nd redox waves were irreversible since the peak potentials difference(ΔE_p) was larger than 60 mV. Electron number of charge transfer from redox processes was obtained to one electron. Molar conductivity(\wedge_M) indicated the non-elctrolyte in acetonitrile. Comproportionation constant($K_c = 1.03$) is obtainable in the range $-1.03 \text{ V} < \Delta E_4 < -1.77 \text{ V}$.

The 1st and 2nd of redox tests exhibited distinctly an only negative and positive potential values at 25 °C, but the 2nd wave was a break down when at the temperatures increasing an only(to 35 °C till 55 °C). The TBT is not easy to be in gaseous phase because of non-volatile properties. A series of temperatures, TBT have demonstrated that it was to be stabilizer from heat. The reduction potential of the temperature in 0.35 % NaCl solution, it conclude that the product of nonelectroactive

and either impedes the reduction of hydrogen ions in salt solution or exposed to a depleted of reactants in the diffusion layer adjacent to the electrode. TBT is not easy to be degradation in aqueous solution in water or seawater. From these results, we was known that TBT is not easy oxidation. The TBT would be a break down above at pH 11.0. Such a phenomenon which occurs in acetonitrile was believed using as solvent or decomposition.

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