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 pollutants\(^5\). 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-Chen 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 lake\(^5\).

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

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>Redox steps</th>
<th>Differential pulse polarography</th>
<th>Cyclic voltammetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(E_{i/2})</td>
<td>(E_{pc})</td>
</tr>
<tr>
<td>TBT</td>
<td>1st wave</td>
<td>-1.01-1.10</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>2nd wave</td>
<td>-1.78-1.84</td>
<td>0.83</td>
</tr>
</tbody>
</table>

\(\Delta E = E_{p} - (E_{1/2})\) (differential-pulse-half-wave potential ; \(1\) (first), \(2\) (second)), \(\Delta E_p (E_{pa} - E_{pc})\) (cyclic voltammetry; peak to peak separation), \(\Delta E_p\) (differential pulse method ; \(E_p^1 - E_p^2\)), \(E_{p/2}\) (half peak potential) ; \(| E_{pc} - E_{pa} |\) (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)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Redox steps</th>
<th>(E_{i/2})</th>
<th>(E_{pc})</th>
<th>(E_{pa})</th>
<th>(\Delta E_p)</th>
<th>(i_{pc})</th>
<th>(i_{pa})</th>
<th>(i_{pa}/i_{pc})</th>
<th>(n) (\land M)</th>
<th>(K_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBT</td>
<td>1st wave</td>
<td>-1.03</td>
<td>-1.12</td>
<td>-1.00</td>
<td>0.12</td>
<td>0.97</td>
<td>1.00</td>
<td>1.03</td>
<td>1.00</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>2nd wave</td>
<td>-1.77</td>
<td>-1.86</td>
<td>0.00</td>
<td>1.85</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

\(i_{pc}\) : cathodic peak current, \(i_{pa}\) : anodic peak current ; \(n\) : electron number of redox reaction ; \(\land M\) : molar conductance ; \(K_c\) : comproportionation constant.
3. Results and Discussion

3.1. Electrochemical Methods and Measurements

Differential pulse polarography (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 Tin(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 coulometry. 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 \( E_1 \) and \( E_p \) values obtained from the DPP and CV methods did not match for all the steps, yet the \( (E_{p2} - E_1) = 0.83 \) V values obtained by the two methods were clearly in good agreement. However, when comparing the \( E_p \) values, the potential values from the CV method indicated a more negative potential (\( E_{p2} = −1.12 \) V; \( E_{p3} = −1.86 \) V) than values (\( E_{p2} = −1.10 \) V; \( E_{p3} = −1.84 \) 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 \( E_p \) value should not be compared with the DPP method. Consequently, the CV method is applied more widely than the DPP method. More important, the \( (E_{11} \) and \( E_{12} \) values obtained by the DPP and CV methods were almost in good agreement \( (\Delta E_{11}) = 0.02 \) V and \( (\Delta E_{12}) = 0.01 \) V.

In general, a good agreement was found with \( \Delta E_k = ±20 \text{ mV}(0.02 \text{ V}) \), as determined by the width of the cyclic voltammetric method. In contrast, the \( \Delta E_p \) 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 \( \Delta E_p \) values were chemically irreversible. As
shown in Table 1, cathodic peak potential (E_p) 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_p values, which were taken as the average between the cathodic and anodic peak potentials. Half wave potentials of the two waves appears at E_p,= -1.03 V of a 1st wave and a E_p,= -1.77 V of a 2nd wave. Fig. 3 obtained from Fig. 2 presents the variation in the half wave potential (E_p) derived from the voltammetric curves relative to temperatures. Considering at 25 °C, the half wave potentials (E_p) 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_p) 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_p values, which were taken as the average between the cathodic and anodic peak potentials. Half wave potentials of the two waves appears at E_p,= -1.03 V of a 1st wave and a E_p,= -1.77 V of a 2nd wave. Fig. 2 shows a reduction 1st wave at E_p,=-1.12 V and an oxidation wave at E_p,= +1.00 V, a reduction 2nd wave at E_p,=-1.86 V and an oxidation wave at E_p,=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 current ratios of the 1st and 2nd wave were i_p,a/i_p,c = 1.03 and i_p,a/i_p,c =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 (∆M) was indicated 0.47, this compound behaviors as nonelectrolyte in acetonitrile solvent with molar conductivities corresponding to the lowest value proposed by Geary. The relation of the concentration at equilibrium is expressed by the comproportionation constant, K_c.

\[ K_c = \exp \left( \frac{\Delta E_p}{RT} \right) \]

where \( n_1 = n_2 = 1 \) (electron number), \( K_c = \exp(\Delta E_p/25.69) \) at 298 K, with that method, value of \( K_c \neq 1.03 \) is obtainable in the range -1.03 V < ∆E_p < -1.77 V. This value is a sufficiently small comproportionation constant(K_c). Myer and Shain have given a curve applicable in the range for the width of a multistep response, (E_p - E_m) vs. ∆E_p. 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 ∆E_p. On the other hand, we can be applied over the whole experimentally accessible range of ∆E_p values. 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 comproportionation 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 ∆E_p values that agree within about ±3 mV. In the region of special
interest (ΔEi < 300 mV), this give Kc values with about a 10%. Assuming that experimental requirements for reversibility and diffusion are met, we estimate that the derived Kc’s are good to within5 10%. It is known that Kc value depend on several energetic factors. Among them (ligand-metal), electrostatic interaction between the redox centers, strongly related to their distance, was believed to make the major contribution9. This indicates that the electrostatic factor is sufficient to explain Kc variations. In this respect, Kc values for diferrocenylenzenes (DFB) and their substituted derivatives shows a higher DFB than TBT (for examples: CH2DFB (Kc = 160), ClDFB (Kc = 35), CH2DFB (Kc = 25), CNDFB (Kc = 20). We was known that Kc was obtained to more small value. This facts was believed to factors above reported.

3.2. Influence of Temperature

Major pathway of organo-tin compounds released to marine environment is via uses as antifouling agents. These compounds except low molecular weight are not easy to be in gaseous phase because of their non-volatile properties. But they are readily adsorbed to particulate matters and its may be removed from water in increased sediment concentration.

In Fig. 3 have been plotted their (E1/2) and (E1) values against at the temperatures. It was based on data Table 3 obtained from redox potentials derived with the voltammogram curves relatives to temperature. This reactions would appear to negative potentials of the all temperatures with exception at 25°C. On the other hand, the redox processes consisted an only two step waves at 15 and 25°C. The 2nd wave was break down when at the temperatures increasing (to 35 till 55°C). The series of redox tests exhibited distinctly an only negative and positive potentials values at 25°C. These waves were occurred with the couples reaction of the 1st, 2nd wave, and single reaction of the 3rd wave as follows at 25°C (1st wave: (E1) = -1.07 V, (E2) = +0.91 V ; 2nd wave: (E1) = -1.77 V, (E2) = +0.65 V ; and 3rd wave: E1 = +0.13 V, respectively)

A series of temperatures, tributyltin compound have demonstrated that it was to be stabilizer from heat.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Temperature(℃)</th>
<th>Temperature(0.35 % NaCl)</th>
<th>pH(25 ℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox steps</td>
<td>(E1/2 ; (V))</td>
<td>(E1/2 ; (V))</td>
<td>(E1/2 ; (V))</td>
</tr>
<tr>
<td>1st wave</td>
<td>15</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>-0.89</td>
<td>-1.07</td>
<td>-1.05</td>
<td>-1.06</td>
</tr>
<tr>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd wave</td>
<td>-1.76</td>
<td>-1.77</td>
<td>0.00</td>
</tr>
<tr>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3. Influence of Temperature for Added Salt

Organo-tin compounds undergo abigeneric 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.

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(E½) 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 tributyltin(CH(CH2)3SnCH=CH2) was expected to displaced by Cl⁻ ion SnCl. 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 E½ vs. pH for redox reaction with tributyltin at 25°C (○ : reduction potential; ▽ : oxidation potential).](image)

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((E½)1=-0.30 V, (E½)2=-0.93 V); pH 5.0((E½)1=-0.34 V, (E½)2=-1.06 V); pH 7.0((E½)1=-0.35 V, (E½)1=0.85 V, (E½)2=-1.07 V, (E½)2=0.66 V); pH 9.0((E½)1=-0.34 V, (E½)1=0.83 V, (E½)2=0.87 V, (E½)2=-1.06 V, (E½)2=0.65 V); pH 11.0((E½)1=-0.37 V, (E½)1=0.88 V, (E½)2=-0.91 V, (E½)2=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(E½) 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 (ΔEp) was larger than 60 mV. Electron number of charge transfer from redox processes was obtained to one electron. Molar conductivity (κM) indicated the non-electrolyte in acetonitrile. Comproportionation constant (Kc = 1.03) is obtainable in the range -1.03 V < ΔE1 < -1.77 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. TBTs 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.

References