Some Electrochemical Studies on the Bionic Nereistoxin Pesticide_\(\text{(CH3)2NHCH(CH2S2O3)2NaH2O}\)

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杀虫单（\(\text{(CH}_3\text{)}_2\text{NHCH(CH}_2\text{S}_2\text{O}_3\text{)}_2\text{Na} \cdot \text{H}_2\text{O}\)）是我国独自开发的一种沙蚕毒系仿生性农药。

我们用循环伏安法和计时库仑法研究了杀虫单的电极反应过程及在电位扫描速率，支持电解质 \(\text{PH}\) 以及浓度变化时对峰电流及峰电位的影响。研究表明杀虫单发生不可逆还原电极反应，还原产物二氢沙蚕毒素在电极上发生强吸附，其吸附量为 \(8.23 \times 10^{-10} \text{ mol/cm}^2\)。在随后的循环电位扫描中二氢沙蚕毒素氧化生成沙蚕毒素在循环伏安图上出现新电流峰。沙蚕毒素与二氢沙蚕素的峰电位相差 \(33 \text{ mV}\)，两者间有 \(2\) 电子可逆电极反应特征。
Some Electrochemical Studies on the Bionic Nereistoxin Pesticide-$(\text{CH}_3)_2\text{NHCH(CH}_2\text{S}_2\text{O}_3)_2\text{Na} \cdot \text{H}_2\text{O}$

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Abstract A study of cyclic voltammetric behavior of the nereistoxin pesticide known as Shachongdan is reported. The effects of scan rate, electrolyte pH, and concentration are discussed. The study shows that this electrode process is an irreversible electrode reaction. The saturation adsorption of dihydronereistoxin on the electrode is also discussed with the saturation adsorption amount of $8.23 \times 10^{-10}$ mol/cm$^2$.

Key words Cyclic voltammetry, Shachongdan, Dihydronereistoxin, Nereistoxin pesticide

The bionic pesticide $(\text{CH}_3)_2\text{NHCH(CH}_2\text{S}_2\text{O}_3)_2\text{Na} \cdot \text{H}_2\text{O}$ is one of the nereistoxin pesticides. It has been broadly used on China, the world’s largest rice production country, under the commercial name Shachongdan and used to protect paddy from snout moth’s larva. Zhang Zeying et al have reported the chemical structure of Shachongdan as a kind of Bunte salt $\text{RS}_2\text{O}_3\text{Na}^{[1]}$. Distler has discussed its synthesis, chemical properties, and its industrial application$^{[2]}$. There is little published about the electrochemical behavior of Shachongdan. The only literature related is about the polarographic behavior of $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}_2\text{O}_3\text{H}$ reported by Strick$^{[3]}$. In this study, The cyclic voltammetric behavior of Shachongdan is reported, and the related electrode process discussed.

1 Experiment

1.1 Apparatus and electrodes

Electrochemical measurements (cyclic voltammetry) were performed with a BAS-100A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) and a Model-303A static mercury drop electrode (EG&G Princeton Applied Research Corporation, Princeton, NJ).

1.2 Reagent and solutions

The Shachongdan pesticide product was recrystallized six times to obtain a purity of more

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than 99%. The supporting electrolyte solution consisted of 0.20 mol·L⁻¹ K₂HPO₄·KH₂PO₄ buffer of pH 6.6. All test solutions were purged with nitrogen to expel the dissolved oxygen before using.

2 Results and Discussion

2.1 Cyclic Voltammetric Behavior of Shachongdan

The cyclic voltammogram is illustrated in Fig. 1 for a 1.0×10⁻³ mol·L⁻¹ solution of Shachongdan in pH 6.6 phosphate buffer at 2.5 cycle scan at potential scan rate of 100 mV·s⁻¹ and scan range of -0.050 V to -1.100 V. As shown in Fig. 1, during the first scan from -0.050 V to -1.100 V only one cathodic peak current is observed with ̂E_{pc1} at -0.782 V. It is due to the reduction of Shachongdan in the aqueous solution as shown below:

\[
\text{CH}_3\text{NCH}_2\text{S}_2\text{O}_3\text{Na} + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{CH}_3\text{NCH}_2\text{SH} + \text{NaHSO}_3 + \text{H}_2\text{SO}_3 \quad (1)
\]

(Shachongdan) (dihydronereistoxin)

One of the products is dihydronereistoxin which contains two thiol groups and can easily from a disulfide at an electrode by an oxidation⁴⁴. Therefore during the second scan from -1.100 V to -0.050 V, the anodic peak corresponding to the oxidation of dihydronereistoxin to nereistoxin is obtained with ̂E_{pa1} at -0.306 V. The stoichiometric equation for the oxidation is following:

\[
\text{CH}_3\text{NCH}_2\text{SH} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{NCH}_2\text{S} + \text{H}_2\text{SO}_3 \quad (2)
\]

(dihydronereistoxin) (nereistoxin)

At a more positive electrode potential another anodic peak shows up with ̂E_{pa2} at -0.212 V. From this complete one cyclic voltammogram which consisted of two opposite potential scans, it is obvious that the reaction (1) is irreversible.

During the second cycle of potential scan from -0.050 V to -1.100 V, besides ̂E_{pc1} which was observed during the first scan, three new cathodic peak currents also appear with ̂E_{pc2} at -0.286 V, ̂E_{pc3} at -0.339 V, and ̂E_{pc4} at -0.515 V, respectively. By comparing with the cyclic voltammogram of nereistoxin standard it is proved that the cathodic peak ̂E_{pc3} (-0.339 V) is caused by the
reduction of nereistoxin, while the cathodic peak $E_{pc4}$ (-0.515 V) is related to the electrode reaction involving $\text{SO}_3^{2-}$. In Fig. 1, the potential difference between the digydroneistoxin oxidation peak $E_{pa1}$ (-0.306 V) and the nereistoxin reduction peak $E_{pa3}$ (-0.339 V) is 33 mV. By comparing with the theoretical value of 29.5 mV (at 25°C) for the potential difference between cathodic and anodic peaks of reversible electrode reactions involving two electrons, it is concluded that the electrode reaction (2) is reversible.

It is noticed that all peak currents, except for $I_{pc4}$ ($E_{pc4}$ at -0.515 V), changed during the first few potential cycles. For example, the cathodic peak current $I_{pc1}$ was 22.3 μA in first scan, but was reduced to 12.6 μA in second and third scan, respectively. During the same time, the cathodic peak current $I_{pc3}$ increased from 5.09 μA to 6.24 μA. During the first two scans, the anodic peak current $I_{pa1}$ increased 24.7% from 3.89 μA to 4.85 μA. After the first two three scans all these peak currents reached stable values and no longer changed with subsequent cycles. This experimental result indicates that adsorption process is may be involved during the electrode reaction. For example, the decrease of $I_{pc1}$ during the first three scan cycles was due to the adsorption of the product digydroneistoxin. The adsorbed digydroneistoxin reduced the effective electrode surface area and blocked the Shachongdan molecules diffusing towards the electrode, and eventually caused a decrease of cathodic currents. When the adsorption and desorption equilibrium was reached after the first few scan cycles, the cathodic peak currents became stable. Based on the same reason, the adsorption of digydroneistoxin led to an increase of its concentration on the surface of the electrode and this caused an increase of anodic peak current $I_{pa1}$ and $I_{pc3}$ during the first two scan cycles.

To verify the above assumptions and explanation for adsorption, the following experiment was designed. First, the 1.0 × 10^{-3} mol·L^{-1} of Shachongdan solution was electrolyzed for 10 seconds at -1.100 V. If the digydroneistoxin can strongly adsorb on the electrode surface, it would actually turn the electrode into a digydroneistoxin modified electrode. The electrode was then transferred to a solution which contained only the supporting electrolyte. The cyclic voltammetric scan was performed starting from -0.400 V and cycling between -0.400 to -0.010 V for seven times as shown in Fig. 2.

It can be seen that even after undergoing seven repetitive cycling there are still some reactant and product residuals left on the surface of the electrode. This experimental observation confirmed the assumption of strong adsorption of digydroneistoxin on the mercury electrode surface. This also provided an explanation for the two small peaks $E_{pa2}$ and $E_{pc2}$ in

![Fig. 2](image_url) Cyclic voltammogram of static mercury drop electrode after digydroneistoxin adsorption
Fig. 1, which are both shown as post-adsorption peaks on the cyclic voltammogram due to the strong adsorption of the product of the electrode reaction\[^{[5]}\].

### 2.2 Effects of Potential Scan Rate

The peak potentials \(E_{p\text{cl}}\), \(E_{p\text{a1}}\) and peak currents \(I_{p\text{cl}}\), \(I_{p\text{a1}}\) at different potential scan rates were collected, and the effect of scan rate was examined as shown in Table 1. It can be seen that as the scan rate increases, \(E_{p\text{cl}}\) shifts toward the negative potential direction while the ratio of \(I_{p\text{cl}}/V^{1/2}\) keeps constant. These coincide with the typical behavior of an irreversible electrode reaction\[^{[6]}\]. It also can be seen that as the scan rate increases, \(E_{p\text{a1}}\) shifts toward the positive potential direction and the ratio of \(I_{p\text{a1}}/V^{1/2}\) gradually decrease. This could be caused by the electrode adsorption.

<table>
<thead>
<tr>
<th>(v/\text{mV} \cdot \text{s}^{-1})</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{p\text{cl}}/\text{mV})</td>
<td>-754</td>
<td>-769</td>
<td>-782</td>
<td>-786</td>
<td>-785</td>
<td>-787</td>
<td>-785</td>
<td>-790</td>
<td>-796</td>
</tr>
<tr>
<td>(I_{p\text{cl}}/\mu\text{A})</td>
<td>11.0</td>
<td>15.7</td>
<td>21.8</td>
<td>26.2</td>
<td>30.0</td>
<td>34.1</td>
<td>37.6</td>
<td>40.7</td>
<td>43.3</td>
</tr>
<tr>
<td>(I_{p\text{cl}}/V^{1/2})</td>
<td>2.20</td>
<td>2.22</td>
<td>2.18</td>
<td>2.15</td>
<td>2.13</td>
<td>2.16</td>
<td>2.17</td>
<td>2.18</td>
<td>2.17</td>
</tr>
<tr>
<td>(E_{p\text{a1}}/\text{mV})</td>
<td>-301</td>
<td>-304</td>
<td>-304</td>
<td>-298</td>
<td>-280</td>
<td>-282</td>
<td>-277</td>
<td>-278</td>
<td>-277</td>
</tr>
<tr>
<td>(I_{p\text{a1}}/\mu\text{A})</td>
<td>1.99</td>
<td>2.81</td>
<td>3.75</td>
<td>4.31</td>
<td>4.71</td>
<td>5.11</td>
<td>5.30</td>
<td>5.42</td>
<td>5.74</td>
</tr>
<tr>
<td>(I_{p\text{a1}}/V^{1/2})</td>
<td>0.398</td>
<td>0.397</td>
<td>0.375</td>
<td>0.353</td>
<td>0.334</td>
<td>0.323</td>
<td>0.306</td>
<td>0.290</td>
<td>0.287</td>
</tr>
</tbody>
</table>

### 2.3 Effects of Solution pH

Since the proton \(H^+\) is involved in both reactions (1) and (2), the solution pH is a factor that affects both peak potential and peak current. As it can be seen from Fig. 3, at pH < 6 the \(E_{p\text{cl}}\) was stable while at pH > 6 the \(E_{p\text{cl}}\) quickly moves to negative direction. When the solution pH falls between 1 to 3, the effect of pH on \(I_{p\text{cl}}\) is not significant, but when the pH > 3 the \(I_{p\text{cl}}\) linearly decrease as the pH increases. The pH affects both peak potential and peak current of all peaks in this study. Especially, since the product of the electrode reaction (1), \(SO_3^{2-}\), can cause a reducing electrode reaction under acidic conditions and the cyclic voltammetric peak shape was sensitively affected at low pH range.

### 2.4 Effects of Concentration

The relation between the concentration of Shachongdan and the peak current is shown in Fig. 4. At all different peak potentials the Ip always increases when concentration increases. Fig. 4 also shows that at the peak potential of \(E_p = -0.212\) V, and as the concentration increases the peak current \(I_p\) increases at low concentration and then reaches a maximum value at a concentration of \(1.80 \times 10^{-3}\) mol/L. This maximum value represents saturate adsorption conditions.
2.5 Determination of Adsorption

The chronocoulometric method was used for the determination of adsorption on the electrode surface. The Shachongdan solution was first electrolyzed at 1.100 V for two seconds to allow the electrode reduction product dihydronereistoxin to adsorb onto the surface of the static mercury drop electrode. A double potential-step chronocoulometric analysis was then performed. A typical Ans on graph (coulomb-time curve) was obtained and is shown in Fig. 5. It can be seen from this $Q-t^{1/2}$ graph that the difference of coulometric intercepts between the forward potential step and backward potential step is 3.33 $\mu$C, indicating a strong adsorption on the electrode by a reaction product.

This experiment has been performed at different concentrations of Shangchongdan. By measuring the differences of coulometric intercepts between the forward potential step and backward potential step from these $Q-t^{1/2}$ graphs of different concentration, a $Q-C$ graph was obtained as shown in Fig. 6. Fig. 6 indicates that the adsorption becomes saturated when the concentration of Shachongdan reaches $1.80 \times 10^{-3}$ mol/L. This conclusion agrees with the experimental result discussed for curve C in Fig. 4. Since $Q = 4.05 \mu$C at saturate adsorption according to Fig. 6, and knowing that the surface area of the static mercury drop electrode is 0.025 5 cm$^2$, the saturate adsorption amount ($\Gamma$) of dihydronereistoxin on the electrode was calculated as equal to $8.23 \times 10^{-10}$ mol/cm$^2$ using the equation $Q = nF\Gamma$. 

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**Fig. 3** Effects of solution pH on peak potential and peak current
- C: 1.0 mmol·L$^{-1}$ Shachongdan
- $v$: 100 mV·s$^{-1}$

**Fig. 4** Relation between concentration and peak current
- A) $E_{pc1} = -0.782$ V
- B) $E_{pc3} = -0.306$ V
- C) $E_{pc2} = -0.212$, $E_{pc3} = -0.339$ V
- $v$: 100 mV·s$^{-1}$
3 Conclusions

The electrochemical reduction of the nereistoxin pesticide Shachongdan, which has a $R_2S_2O_3H(Na)$ structure, coincides with the following general reaction. This electrode process is an irreversible electrode reaction.

$$RSH_2S_2O_3Na + 2H^+ + 2e \rightarrow RSH + NaHSO_3$$

There is a strong adsorption on the electrode by the reaction product dihydronereistoxin with the saturate adsorption amount of $8.23 \times 10^{-10}$ mol/cm$^2$.

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