

# 吡虫啉电化学性能研究

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**摘要:** 应用循环伏安法研究了吡虫啉(IDP)在玻碳电极的电化学行为. 结果表明: IDP的还原反应是不可逆的, 且受扩散控制, 电子转移数4, 扩散系数  $D_R$   $2.44 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ , 反应活化能  $E_d$   $9.33 \text{ kJ} \cdot \text{mol}^{-1}$ .

**关键词:** 吡虫啉; 电化学; 循环伏安法; 线性扫描伏安法

**中图分类号:** O646

**文献标识码:** A

吡虫啉(Imidacloprid, IDP)是德国和日本1984年共同开发的一种新烟碱类杀虫剂, 具有低毒、高效、有效期长且不易产生抗药性, 使用过程对人、畜均较安全等特点<sup>[1-2]</sup>. IDP的分子结构如图1. 它是烟碱乙酰胆碱受体的抑制剂, 作用于昆虫神经<sup>[3-4]</sup>, 对防治危害水稻、小麦、果树、蔬菜的飞虱、叶蝉、蚜虫等刺吸式口器害虫有特效<sup>[5-7]</sup>, 目前已在许多国家广泛使用<sup>[8]</sup>. deErenchun等曾以电化学方法研究了IDP在使用过程中于土壤与水中的残留量<sup>[9-11]</sup>. 本文应用循环伏安法研究水溶液中IDP的电化学特性, 以期对IDP检测提供依据.

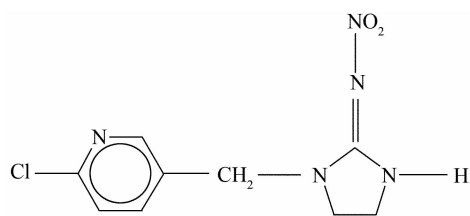


图1 IDP的分子结构

Fig. 1 Molecular structure of imidacloprid (IDP)

## 1 实验部分

### 1.1 主要试剂和仪器

吡虫啉(95%), 其他试剂均为分析纯.

在100 mL磷酸、硼酸和醋酸(浓度各为  $0.04 \text{ mol} \cdot \text{L}^{-1}$ )混合液中加入不同体积的氢氧化钠( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ), 配成pH 1.8 ~ 11.9的伯瑞坦-

罗宾森(B-R)缓冲溶液.

电化学工作站 CHI660a(上海振华), PHSJ-3F pH计(上海雷磁).

### 1.2 电极体系与测试

夹套式电解池, 三电极体系由玻碳工作电极( $\phi = 3 \text{ mm}$ )或 Model 616型旋转圆盘电极( $\phi = 5 \text{ mm}$ , RDE, 经  $0.03 \mu\text{m} \alpha\text{-Al}_2\text{O}_3$  抛光, 二次水冲洗)和饱和甘汞电极(SCE, 参比电极)、铂丝对电极与IDP缓冲溶液组成. 通氮除氧10 min后进行循环伏安测试.

## 2 结果与讨论

### 2.1 IDP的循环伏安曲线

图2给出IDP在B-R缓冲溶液(pH = 7.0)中于玻碳电极上的循环伏安曲线(25 °C, 扫描速率  $0.1 \text{ V} \cdot \text{s}^{-1}$ , 电位区间  $0 \sim -1.4 \text{ V}$ ). 从图看出, 在空白B-R缓冲溶液中, CV曲线(b)不出现电化学反应峰. 而加入IDP后在  $-1.2 \text{ V}$  左右观察到一个还原峰(曲线a), 对应于IDP硝基的还原.

图3为IDP在上述缓冲溶液中于玻碳电极上多周扫描的CV曲线. 如图, 随着循环次数的增加, 峰电流逐渐下降, 最后达到稳定. 这可能是还原产物在电极表面累积所致.

图4给出不同扫描速率下IDP的CV峰电流随溶液pH的变化. 可以看出, 对不同的扫速, 峰电流均以溶液pH约为9时强度最大.

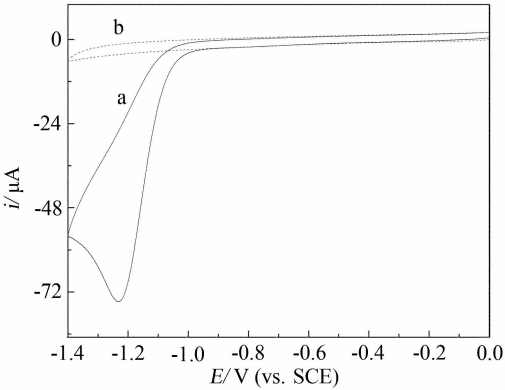


图 2 IDP 于 B-R 缓冲液(pH 7.0)玻碳电极上的循环伏安曲线( $0.1\text{ V} \cdot \text{s}^{-1}$ ,  $25\text{ }^{\circ}\text{C}$ )  
a.  $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$  IDP + B-R 缓冲溶液; b. B-R 缓冲溶液

Fig. 2 Cyclic voltammograms of IDP at GC electrode in pH 7.0 B-R buffer( $0.1\text{ V} \cdot \text{s}^{-1}$ ,  $25\text{ }^{\circ}\text{C}$ )  
a.  $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$  IDP + B-R buffer; b. B-R buffer

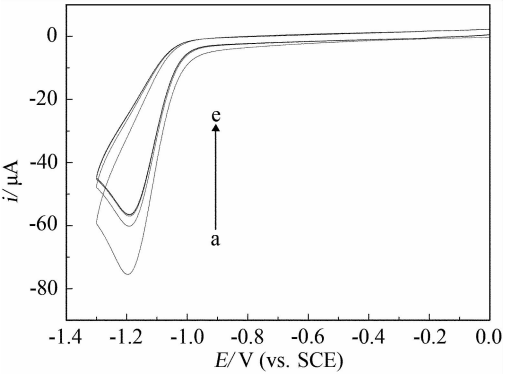


图 3 IDP ( $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) 在 B-R 缓冲溶液中 (pH 7.0) 于玻碳电极上的多周扫描循环伏安曲线( $0.1\text{ V} \cdot \text{s}^{-1}$ ,  $25\text{ }^{\circ}\text{C}$ )

Fig. 3 CV curves of the IDP ( $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) in B-R buffer solution (pH 7.0) at GC electrode with multi-cycles ( $0.1\text{ V} \cdot \text{s}^{-1}$ ,  $25\text{ }^{\circ}\text{C}$ )  
Cyclic number(a ~ e): 1; 2; 3; 4; 5

2.2 IDP 还原反应参数

图 5 给出在 pH 7.0 的 B-R 缓冲溶液( $25\text{ }^{\circ}\text{C}$ )中不同扫描速率下 IDP ( $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) 于玻碳电极上的循环伏安曲线.

从图看出,还原峰电流和峰电位都随扫描速率而变化. 据 Nicholson 公式,对不可逆还原反应有:

$$E_p = E^{0'} + \frac{RT}{\alpha n_a F} \left[ 0.781 + \ln \left( \frac{D_R^{1/2}}{k^0} \right) + \ln \left( \frac{\alpha n_a F \nu}{RT} \right)^{1/2} \right] \quad (1)$$

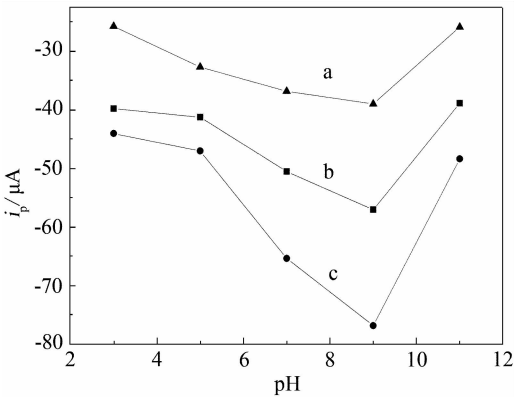


图 4 IDP( $25\text{ }^{\circ}\text{C}$ ,  $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) 的  $i_p \sim \text{pH}$  关系  
Fig. 4 Relationship between the peak current  $i_p$  and solution pH for IDP ( $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) at GC electrode with different scan rates at  $25\text{ }^{\circ}\text{C}$   
Scan rate(a ~ c)/ $\text{V} \cdot \text{s}^{-1}$ : 0.02; 0.05; 0.1

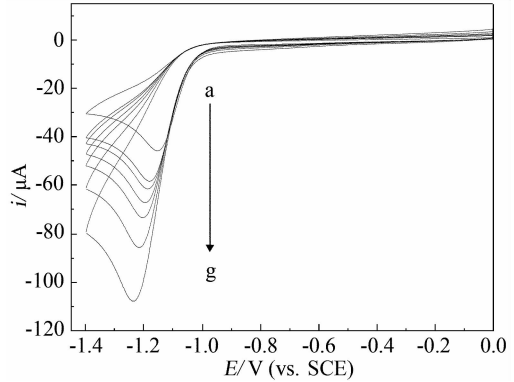


图 5 IDP ( $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) 于玻碳电极上不同扫描速率的 CV 曲线  
Fig. 5 CV curves of the IDP ( $1.56 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ) in B-R buffer solution (pH 7.0) at GC electrode with different scan rates at  $25\text{ }^{\circ}\text{C}$   
Scan rate (a ~ g)/ $\text{V} \cdot \text{s}^{-1}$ : 0.02; 0.05; 0.06; 0.08; 0.1; 0.15; 0.25

式中: $E^{0'}$  为形式标准电位,  $R$  为气体常数,  $n_a$  为电子转移数,  $\alpha$  为电子转移系数,  $F$  为法拉第常数,  $T$  为绝对温度. 以  $E_p$  对  $\ln \nu$  作图, 即如图 6 所示, 证实此处 IDP 的电化学反应是一不可逆的过程. 从图中直线斜率求得  $\alpha n_a = 0.37$ . 假设决速步骤的电子转移数  $n_a = 1$ , 则  $\alpha = 0.37$ , 符合一般电极反应中  $\alpha$  的取值范围  $0.3 \sim 0.7$ . 如取  $n_a = 2$ , 则  $\alpha = 0.18$ , 与其通常表现值相悖. 据此, 该反应决速步骤的电子转移数应当为 1.

对由扩散控制的不可逆电极反应  $i_p$  有:

$$i_p = - (2.99 \times 10^5) n (\alpha n_a)^{1/2} A C_R D_R^{1/2} \nu^{1/2} \quad (2)$$

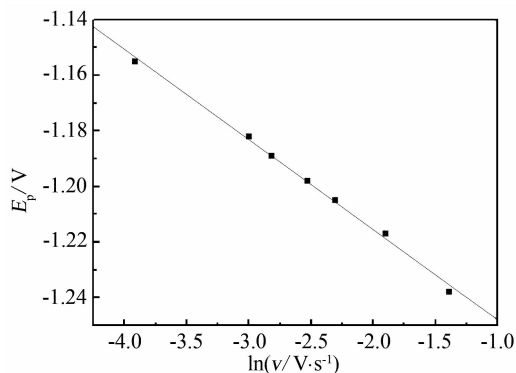


图6 依据图5得到的IDP在B-R缓冲溶液(pH 7.0)中玻碳电极上的 $E_p \sim \ln v$ 变化关系图

Fig. 6 Relationship between the peak potential  $E_p$  and  $\ln v$  for IDP in B-R buffer solution (pH 7.0) at GC electrode based on Fig. 5

式中: $A$ 为电极面积, $C_R$ 为IDP浓度.参照图5,图7表明IDP的CV扫描中,峰电流 $i_p$ 与扫速平方根 $v^{1/2}$ 呈线性关系.可知该电极反应受扩散控制.据式(2),从直线斜率可得 $nD_R^{1/2} = 6.66 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1/2}$ .

图8给出在pH 7.0的B-R缓冲溶液(25℃)中IDP( $1.56 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ )于旋转圆盘电极上不同转速下的线性扫描伏安曲线.从图看出,当电位从-0.6 V扫描至-1.55 V时,极限电流 $i_l$ 随着转速的增加而增加.

根据Levich方程式:

$$i_{l,c} = 0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_0^* \quad (3)$$

式中: $i_{l,c}$ ,极限扩散电流; $n$ ,电子转移数; $A$ ,旋转圆盘电极面积; $C_0^*$ ,IDP浓度; $D_R$ ,扩散系数; $\omega$ ,角速度; $\nu$ ,动力黏度; $F$ ,法拉第常数.根据式(3),以 $i_{l,c}$ 对角速度平方根( $\omega^{1/2}$ )作图,呈现良好的线性关系,如图9所示.表明IDP在玻碳电极上的还原反应主要受扩散控制.由图9直线斜率可得 $nD_R^{2/3} = 7.70 \times 10^{-4} \text{ cm} \cdot \text{s}^{-1/2}$ .又已知 $nD_R^{1/2} = 6.66 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1/2}$ ,求得 $D_R = 2.44 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1/2}$ , $n = 4.27$ ,说明IDP在玻碳电极上的反应为4电子反应.其电极反应式为<sup>[12]</sup>:

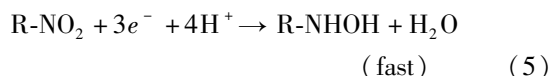


图10示出在 $0.1 \text{ V} \cdot \text{s}^{-1}$ 扫速、不同温度下的IDP循环伏安曲线.如图,升高温度,峰电流上升,峰电位负移.电极反应扩散系数与温度变化关系

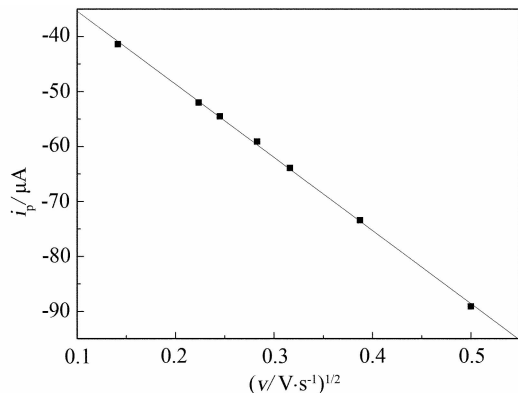


图7 依据图5得到的IDP的 $i_p \sim v^{1/2}$ 变化曲线

Fig. 7 Relationship between the peak current  $i_p$  and  $v^{1/2}$  for the IDP at GC electrode based on Fig. 5

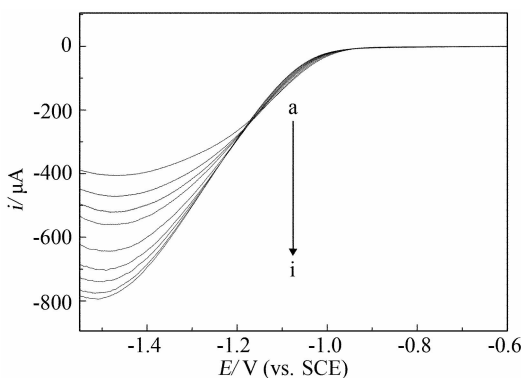


图8 IDP( $1.56 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ )于旋转圆盘电极上不同转速下的线性扫描伏安曲线

Fig. 8 LSV curves of IDP( $1.56 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) on the rotating GC electrode  
Electrolyte: B-R buffer solution (pH 7.0, 25℃), rotating rate (a ~ i)/ $\text{r} \cdot \text{min}^{-1}$ : 400; 600; 800; 1000; 1500; 2000; 2500; 3000; 3500

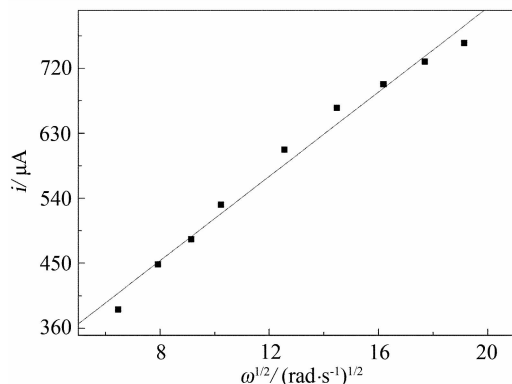


图9 依据图8得到的IDP在B-R缓冲溶液(pH 7.0)中旋转圆盘电极上的 $i \sim \omega^{1/2}$ 变化关系图

Fig. 9 Relationship between  $i$  and  $\omega^{1/2}$  for IDP in B-R buffer solution (pH 7.0) at rotating GC electrode from Fig. 8

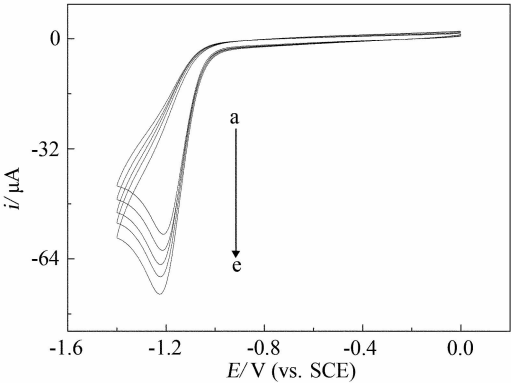


图 10 IDP( $1.56 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) 在 pH 7.0 B-R 缓冲溶液中 GC 电极不同温度下的 CV 曲线

Fig. 10 CV curves of the IDP in B-R buffer solution (pH7.0) at GC electrode with different temperatures  
 $t(a \sim e)/^{\circ}\text{C}$ : 30; 35; 40; 45; 50, scan rate: 0.1  $\text{V} \cdot \text{s}^{-1}$

如下:

$$\log D = -\frac{E_d}{2.303RT} + \log D_0 \tag{6}$$

式中: $E_d$ ,反应活化能; $D_0$ ,扩散系数(25 °C);  
 $R$ ,气体常数; $T$ ,绝对温度.

图 11 给出 IDP 的还原峰电流对数随  $T^{-1}$  的变化关系曲线,扫速为  $0.1 \text{ V} \cdot \text{s}^{-1}$ . 据图,从直线斜率可求得反应活化能  $E_d$   $9.33 \text{ kJ} \cdot \text{mol}^{-1}$ .

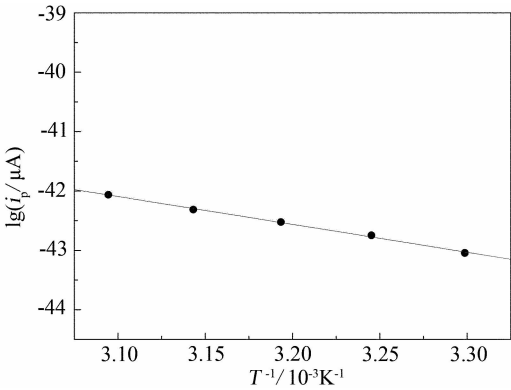


图 11 IDP  $\lg i_p \sim T^{-1}$  变化(参照图 10)

Fig. 11 The relationship between  $\lg i_p$  and  $T^{-1}$  from Fig. 10

### 3 结 论

在 25 °C, pH = 7 的缓冲溶液中, IDP 于玻碳电极上的还原反应是不可逆的, 其反应受扩散控制. 电子转移数 4, 扩散系数  $D_R$   $2.44 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ , 反应活化能  $E_d$   $9.33 \text{ kJ} \cdot \text{mol}^{-1}$ .

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## Electrochemical Behavior of Imidacloprid

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**Abstract:** The electrochemical behavior of imidacloprid (IDP) on glassy carbon electrode has been investigated by cyclic voltammetry. The result shows that the electrochemical reduction of IDP is irreversible and controlled by diffusion. At 25 °C, the numbers of the electrons transferred of IDP in the electrochemical reaction are four. The diffusion coefficient of IDP is  $2.44 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$  and the diffusion activation energy is calculated to be 9.33 kJ · mol<sup>-1</sup>.

**Key words:** imidacloprid; electrochemistry; cyclic voltammetry; linear sweep voltammetry