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Full Length Research Paper

## Polarographic Behaviour and Analysis of Permethrin

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### Abstract

The electrochemical reduction behaviour of Permethrin has been carried out, by employing d.c. polarography, cyclic voltammetry (CV) and differential pulse polarography (DPP) in the supporting electrolytes of the pH ranging from 2.0 to 12.0. The nature of electrode process was studied, the number of electrons was evaluated and the reduction mechanism was proposed. Kinetic parameters such as transfer coefficient, diffusion coefficient and heterogeneous forward rate constant are evaluated and reported. Quantitative determination was carried out in the concentration range  $1.5 \times 10^{-5}$  M to  $2.5 \times 10^{-8}$  M using a differential pulse polarographic method, with a lower detection limit of  $2.0 \times 10^{-8}$  M. The propounded technique was successfully applied in the quantitative estimation of Permethrin in various agricultural formulations using standard addition and calibration method.

**Key words:** Permethrin, Polarographic Techniques, Mechanism, Analysis, Agricultural formulations

### Introduction

Pesticides have become an important group of environmental pollutants and may be which are reported to be mutagenic. Introduced commercially less than 20 years, Synthetic pyrethroids now account for more than 30% insecticide used worldwide in agricultural, domestic and veterinary applications [1, 2]. These halogenated and lipophilic compounds are generally recognized as potent neurotoxicants, characterised by high insecticidal properties and low mammalian toxicity [3]. Pyrethroids are highly effective insecticides used for the control of a wide spectrum of insect pests, in agriculture, public areas and household [4]. Pyrethroid insecticide Permethrin [3-Phenoxybenzyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-cyclopropane carboxylate.] (Figure I). Current uses of Permethrin include insecticide, germicide and wood preservative. It acts on the nervous system of insects. It interferes with sodium channels to disrupt the function of neurons and causes muscles to spasm, culminating in paralysis and death [5, 6]. It is highly toxic to some non-target organisms such as honeybees, fish and aquatic invertebrates due to disruption of sodium channels.

A wide range of analytical technique has been applied to the analysis of different pyrethroid insecticides in water, soil and vegetables [7, 8]. Progress obtained with pulse techniques has increased the range of practical applications of voltammetry by enabling determinations of electroactive species at lower concentrations [9]. Electroanalysis of pyrethroid insecticides was performed using different electrodes [10-14]. Since such analytical processes require many steps, they are not only labour-intensive but also time consuming. Therefore, development of a sensitive, convenient and economical electroanalytical method is required for the analysis of pyrethroid residues in agricultural formulations.

In the present work the attention has been on electrochemical study of Permethrin pesticide to get more information on the reduction mechanism of the compound and the electrode kinetics concerned, employing advanced electrochemical techniques. Since the application of electrochemistry to the Permethrin pesticide is very limited. It is chosen to get more information on the electrode kinetics as well as reduction mechanism of olefinic ( $>C=C<$ ) group by employing advanced electrochemical techniques such as d.c.polarography, cyclic voltammetry, and differential pulse polarography. A rapid, simple and sensitive differential pulse polarography method has been applied to determine the Permethrin pesticide in environmental samples.

### Materials and Methods

A Metrohm unit: E 506 polarecord coupled with E 612 VA-scanner, E 648 VA-combistand, E 608 VA-controller, and a digital electronics 2000 X-Y/t recorder are used for cyclic voltammetric and differential pulse polarographic measurements. All the electrochemical measurements are carried out with three-electrode design at  $25 \pm 0.1^\circ\text{C}$ . The DME (area:  $0.0223 \text{ cm}^2$ , flow rate of Hg:  $2.73 \text{ mg/sec}$ , and mercury column height:  $35 \text{ cm}$ ) and HMDE (with an area of  $0.0328 \text{ cm}^2$ ) are used as working electrodes. Ag/AgCl (s), Cl<sup>-</sup> electrode is used as reference electrode for cyclic voltammetry and differential pulse polarography. Platinum electrode is used as counter electrode for both the techniques. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode, and spot galvanometer, was used for controlled potential electrolysis.

Permethrin was obtained from Rhone-Poulenc (India) Ltd., Mumbai. The purity of the sample was tested by melting point determination and TLC analysis. Britton-Robinson buffers of pH 2.0 to 12.0 were prepared by using 0.2 M boric acid, 0.05 M citric acid, and 0.1 M trisodium orthophosphate. All the chemicals used are of pure analar grade. Stock solution of Permethrin was prepared by dissolving the required amount in methanol and making up to volume with the supporting electrolyte to obtain the desired concentration. Before running the voltammograms the test solution was purged with purified nitrogen for 10 min. A 0.02% aqueous solution of Triton X-100 was used to eliminate the polarographic maxima.

A standard stock solution ( $1.5 \times 10^{-3}$  M) of the compound was prepared by the dissolution of the appropriate amount of the Permethrin pesticide in double distilled water. A 10 ml of the solution (9 ml of the supporting electrolyte + 1 ml of unknown concentration of the depolarizer) is transferred into a polarographic cell and polarogram is recorded after complete deaeration for 15 min. After obtaining the polarogram, small increments (0.2 ml) of the standard solution of electroactive species is added to the cell, deaerated for 1 min. and the polarogram is again recorded under similar conditions. In the same manner, 10 polarograms are recorded for 10 standard additions. The amount of unknown species is calculated by using relevant equation. In the present study the best conditions are obtained at pH 2.0 with a drop time 2 sec, a pulse amplitude 50 mV and applied potentials of -1.02 V for Permethrin. The relative standard deviations and correlation coefficients are found to be 1.21% and 0.963.

## Results & Discussion

### Characterization of wave/peak

The electrochemical behaviour of Permethrin has been studied over the pH range 2.0 to 12.0. A single well defined wave/peak is found in all the techniques in acidic media ( $\text{pH} \leq 4$ ). The typical voltammograms obtained is shown in Figures.II to IV. The wave/peak is attributed to the reduction of the olefinic group ( $>\text{C}=\text{C}<$ ) to the corresponding saturated product in a two electron process.

### Nature of the electrode process

The diffusion controlled adsorption free nature of the electrode process in both the compounds is evidenced from the linear plots of  $i_d$  vs.  $t^{1/2}$  (Figure V) passing through origin in all the supporting electrolytes ranging from pH 2.0 to 12.0. The experimental constancy  $i_p/v^{1/2}$  with scan rate ( $v$ ) in cyclic voltammetry indicates that the electrode process is free from any kinetic complications.

The reduction process is found to be irreversible for Permethrin as evidenced from the disobedience of Tomes' criterion, log-plot analysis and dependence of  $E_{1/2}$  with the concentration of electroactive species in d.c. polarography, the absence of anodic peak in the reverse direction and the variation of peak potential with scan rate in cyclic voltammetry. The marginal variation of peak potential ( $E_m$ ) with concentration and nonlinearity in the plots of  $i_m$  vs.  $1-\sigma / 1+\sigma$  in differential pulse polarography also confirms the irreversible nature of the electrode process.

The half-wave and peak potentials of the experimental compound Permethrin was seen to have shifted towards more negative potentials with increase in pH of the buffer solution indicating the participation of protons in the reduction process. The number of protons involved in the rate determining step is calculated from  $E_{1/2}$  vs. pH plots and is found to be one for permethrin in the reduction processes.

### Identification of the products

Comparison of wave heights of Permethrin in millicoulometry has indicated the number of electrons involved in the electrode process as two in acidic (pH 2.0) and basic media (pH 12.0). Controlled potential electrolysis is carried out with mercury pool cathode, saturated calomel electrode as reference electrode and platinum wire electrode as counter electrode. About 50 mg of the electroactive species under investigation is dissolved in a minimum amount of methanol and added to the cell containing supporting electrolyte (pH 4.0). The applied potentials are fixed at -0.50 V for Permethrin. The electrolysis is carried out approximately for 4 hrs. The product formed after controlled potential electrolysis is identified as the corresponding saturated derivative of olefinic group ( $>\text{C}=\text{C}<$ ) by IR spectral studies (absence of C=C stretching absorption band at  $1695 \text{ cm}^{-1}$ ).

### Kinetic data

The typical kinetic parameters of the electrode process calculated at various pH values in different techniques are presented in Tables I to V. The adsorption free nature of the electrode process is clearly evidenced from the nearly equal diffusion coefficients values obtained from all the techniques for the compound Permethrin. The diffusion coefficient values are seen to be decreased gradually, which account for the decrease in diffusion current with increase in pH due to less availability of protons.

The rate constant values obtained for the reduction of Permethrin in an acidic medium from all the techniques are found to be high indicating that the rate of reaction is fast in acidic solutions due to the fact that the involvement of protons is high. In basic medium, the reduction process does not easily occur owing to the less availability of protons. Therefore, lower rate constant values are obtained.

**Table I.** Typical d.c.polarographic data of Permethrin, Concentration: 0.5 mM, Drop time: 3 Sec

pH	$\frac{-E_{1/2}}{V}$	$\frac{i_d}{\mu A}$	$\alpha n_a$	$\frac{D \times 10^6}{cm^2 s^{-1}}$	$\frac{k_{f,h}^0}{cm s^{-1}}$
2.0	0.36	5.0	0.61	4.56	$3.28 \times 10^9$
4.0	0.47	4.7	0.65	3.78	$2.91 \times 10^{11}$
6.0	0.60	4.4	0.58	3.32	$6.81 \times 10^{12}$
8.0	0.72	4.1	0.51	3.23	$8.74 \times 10^{14}$
10.0	0.81	3.8	0.41	3.05	$3.82 \times 10^{17}$
12.0	0.98	3.6	0.47	2.89	$1.51 \times 10^{19}$

**Table II.** Typical cyclic voltammetric data of Permethrin, Concentration: 0.5 mM, Scane rate: 40 mVs<sup>-1</sup>

pH	$\frac{-Ep}{V}$	$\frac{i_p}{\mu A}$	$\alpha n_a$	$\frac{D \times 10^6}{cm^2 s^{-1}}$	$\frac{k_{f,h}^0}{cm s^{-1}}$
2.0	0.36	4.9	0.63	4.59	$3.92 \times 10^{10}$
4.0	0.47	4.4	0.61	3.68	$9.49 \times 10^{12}$
6.0	0.55	4.2	0.65	3.20	$6.70 \times 10^{13}$
8.0	0.71	3.9	0.60	3.11	$1.31 \times 10^{15}$
10.0	0.82	3.7	0.52	3.02	$3.12 \times 10^{18}$
12.0	0.94	3.4	0.42	2.49	$2.67 \times 10^{20}$

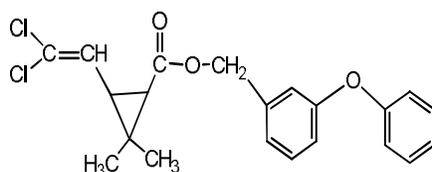
**Table III.** Typical differential pulse polarographic data of Permethrin, Concentration: 0.5 mM, Droptime: 2 Sec, Pulse amplitude: 50 mV

pH	$\frac{-E_m}{V}$	$\frac{i_m}{\mu A}$	$\alpha n_a$	$\frac{D \times 10^6}{cm^2 s^{-1}}$	$\frac{k_{f,h}^0}{cm s^{-1}}$
2.0	0.36	5.1	0.69	4.44	$2.03 \times 10^9$
4.0	0.49	4.7	0.65	3.65	$2.28 \times 10^{10}$
6.0	0.55	4.2	0.67	3.31	$7.26 \times 10^{11}$
8.0	0.63	3.9	0.61	3.23	$5.53 \times 10^{13}$
10.0	0.73	3.7	0.51	3.11	$8.84 \times 10^{16}$
12.0	0.96	3.3	0.48	2.84	$3.78 \times 10^{18}$

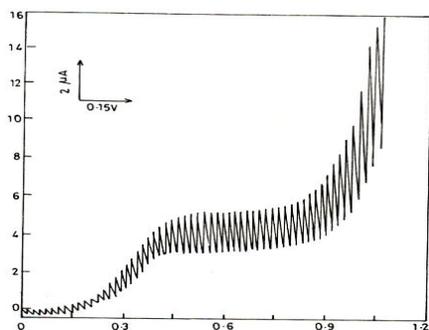
**Table IV.** Determination of Permethrin in agricultural formulations in pH 4.0 Pulse amplitude : 50 mV, Drop time: 1.4 Sec

Sample	Labelled amount (mg)	Amount found* (mg $\pm$ SD)	Average recovery (%)
Baythroid	50	49.60 $\pm$ 0.012	99.20
Baygon	50	49.40 $\pm$ 0.018	99.80
Softac	50	49.00 $\pm$ 0.015	98.00
Baythroid	100	99.89 $\pm$ 0.022	99.89
Baygon	100	99.70 $\pm$ 0.027	99.70
Softac	100	99.65 $\pm$ 0.019	99.65

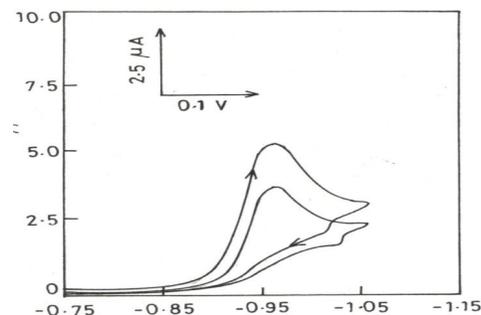
\*Each value is an average of four determinations.



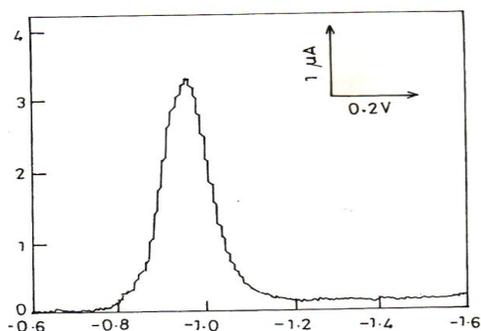
**Figure 1.** Structure of Permethrin



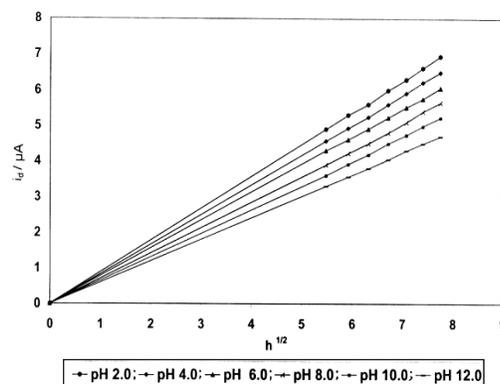
**Figure 2.** Typical d.c polarogram of Permethrin in pH 2.0  
Concentration : 0.5 mM, Drop time: 3 Sec,



**Figure 3.** Typical cyclic voltammogram of Permethrin in pH 4.0  
Concentration : 0.5 mM Scan rate : 40 mVs-1



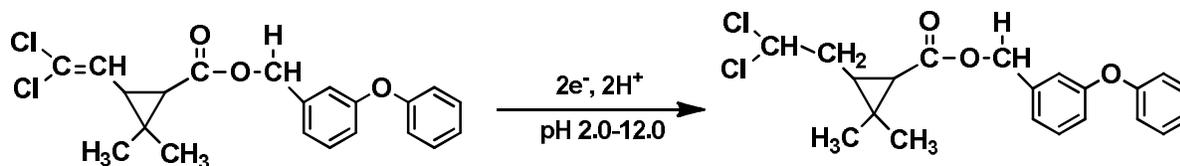
**Figure 4.** Typical differential pulse polarogram of Permethrin in pH 12.0  
Concentration : 0.5 mM, Drop time : 2 Sec, Pulse amplitude: 50 mV



**Figure 5.**  $i_d$  vs.  $h^{1/2}$  plots of Permethrin, Concentration : 0.5 mM

### Electrode mechanism

Based on the above results and observations obtained in the present investigation, as well as from the literature [15, 16] the following reduction mechanism may be proposed for the above compound in the entire pH range:



**Scheme 1:** Electrode mechanism of Permethrin

### Analysis

In the present investigation differential pulse polarography has been employed to work out analytical procedures for the estimation of Permethrin in agricultural formulations using both calibration and standard addition methods. Investigated compounds are found to

exhibit well resolved peaks in pH 4.0 and are chosen for quantitative studies. The peak currents are found to vary linearly with the concentration of the depolariser over the concentration range  $1.5 \times 10^{-5}$  M to  $2.5 \times 10^{-8}$  M for Permethrin. The lower detection limits are found to be  $2.0 \times 10^{-8}$  M for the respective compound, which are calculated from the expression  $dl = 3Sd/m$  where dl is the lower detection limit, Sd is the standard deviation and m is the slope of the calibration plot.

### Recommended analytical procedure

The standard stock solution ( $1 \times 10^{-3}$  M) of Permethrin is prepared by dissolving the required quantity of the electroactive species in methanol. 1 ml of the standard solution is transferred into a polarographic cell and made up with 9 ml of the supporting electrolyte and the solution is purged with oxygen free nitrogen gas for 10 min. After recording the polarograms, small increments (0.2 ml standard solution) are added and the polarograms are recorded after each addition under similar conditions. The optimum conditions for the analytical determination of Permethrin is at pH 4.0 are found to be a drop time 2 sec, pulse amplitude 50 mV and applied potentials of -0.49 V. The relative standard deviations and correlation coefficients for 10 replicates are found to be 1.23% and 0.996 for Permethrin. This method is successfully employed for the determination of the compound in different agricultural formulations.

In the present analysis, a different agricultural formulation Baythroid, Baygon and Softac of Permethrin was chosen. The required quantity of formulations corresponding to a stock solution of concentration  $1 \times 10^{-3}$  M is accurately measured and transferred into a 100 ml calibrated flask containing 50 ml of Methanol. A solution of  $1 \times 10^{-5}$  M is prepared by diluting this stock solution with the buffer solution and the above described procedure is employed. Assay results for the selected formulations are given in Tables I to IV.

### Conclusion

The work describes the voltammetric behaviour of Permethrin based on the reduction of olefinic group of at dropping mercury electrode and hanging mercury drop electrode. The recovery result shows that differential pulse polarography is a simple, reliable and inexpensive method for the determination of Permethrin in formulations. The main advantage of the proposed method over the other ones is that the excipients do not interfere and a separation procedure is not necessary. Differential pulse polarography is employed for the analysis of the title compounds. Analytical procedures are described for quantitative estimation of the compounds in agricultural formulations using both standard addition and calibration methods. The detection limits are found to be  $10^{-8}$  M levels for Permethrin.

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### References

- Best, G. (1995) Pesticides, Developments, Impacts and Controls, The Royal Society of Chemistry, Cambridge
- Davies, J.H. (1985) In The Parathroid Insecticides, J.P. Leahey (Ed.), pp. 1–41, Taylor & Francis, London.
- Velmunegan, B. Ambrose, T. and Selvanayagam, M. (2006) Journal of Environmental and Biology. 27 247.
- Oudou, H.C. Alonso, R.M. and Hansen, H.C.B. (2004) Analytica Chimica Acta., 523, 69.
- Cox, C. (1998) Journal of Pesticide Reform. 18, 14.
- Shan, G. Leeman, W.R. Chang, D.P.Y. and Hammock, B.D. (2000) Journal of Agriculture and Food Chemistry. 48, 4032.
- Leng, G. and Gries, W. (2005) Journal of Chromatography. B. 814, 285.
- Leng, G. Grives, W. and Selim, S. (2005) Toxicol Letter. 162 195.
- Oudou, H.C. Alonso, R.M. Jimenez, R.M. (2001) Electroanalysis, 13, 72.
- Coomber, D.C. Tucker, D.J. Bond, A.M. (1998) Journal of Electroanalytical Chemistry. 10, 163.
- Coomber, D.C. Tucker, D.J. Bond, A.M. (1997) Journal of Electroanalytical Chemistry. 430, 215.
- Coomber, D.C. Tucker, D.J. Bond, A.M. (1997) Journal of Electroanalytical Chemistry. 426, 63.
- Coomber, D.C. Tucker, (1996) Analytical Chemistry 68, 1267.
- Thriveni, T. Rajesh Kumar, J. Lee J.Y and Sreedhar, N.Y. (2009) Food Analytical Methods. 2 66.
- Subbalakshamma, M. Reddy, S.J. (1994) Electroanalysis. 6, 521.
- Sreedhar, N.Y. Reddy, P.R.K. Reddy, G.V.S. and Reddy, S.J. (1997) Talanta. 14, 1859.