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Electrochemical reduction behaviour of valone and determination of its residues in water samples

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ABSTRACT

The present work describes the electrochemical behaviour of valone the carbonyl group containing pesticide and its remains in water samples. Differential pulse polarographic method were used to study the reduction behaviour of valone. Dropping mercury electrode was used as working electrode and universal buffer with pH range2to6 as supporting electrolyte. Reduction mechanism evoluted by cyclic voltammetry. The optimum pH to get well defined peak for the detection is found to be 4.0. The peak current is found to vary linearly with the concentration of the pesticide over the range 1.0 x 10^{-3}M to 1.0 x 10^{-5}M. The lower detection was limit found to be 1.0 x 10^{-5}M.

KEYWORDS

Valone;
Differential pulse
Polarographic method;
Dropping mercury electrode;
Universal buffer;
Water samples.

INTRODUCTION

The term pesticides includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thining fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transfer[1]. Pest is any species that competes with human being for food, invades lawns and gardens, destroys wood in houses, and spreads disease or simply a nuisance. Worldwide about 100 species of plants, (which one calls weeds); animals (mostly insects), fungi and microbes (which can infect crop plants and livestock animals) cause about 90% of the damage to the crops. Insects cause much of the damage to the crops. Valone is a carbonyl group containing rodenticide (2-(3-methylbutanoyl)-1*H*-indene-1,3(2*H*) -dione)which is used to control rodents. Due to the continuous increase in the application of such pesticide, the necessity of water analysis is always growing. The traditional techniques used for such purpose are liquid chromatography and gas chromatography with electron capture detection, which is one of the most adequate due to the very low value obtainable for the detection limit[2]. Reported SPE and HPLC/DAD method to determine pesticide residues in water[3]. Reported GLC, HPLC/DAD and TLC for determination of 51 common pesticides[4]. Employed SPE and HPLC photo diod array detection for determination of pesticide residues in water samples[5]. Reported SMPE/HPLC method for analysis of pesticide residues from straw berries.

So far we have not come across any such study in the literature on the electrochemical reduction behaviour of valone. There fore, we have under taken the present work to establish the experimental conditions for under standing the electro chemical behaviour of valone from the measurement of cyclic voltammetry,differential pulse polarography, controlled potential electrolysis and milli coulometry. It is also aimed to develop DPP method for analysis of valone in its pure form and in spiked water samples.

EXPERIMMENTAL

Apparatus and electrodes

Polarographic assays were performed using a model 364 polarographic analyzer supplied by Princeton applied research corporation,(Princeton,NJ USA)coupled with a kipp and zonen BD8x-t recorder. A dropping mercury electrode (DME) was used as working electrode and a saturated columel electrode (SCE) as the reference electrode. Differential pulse polarograms were recorded with a unit supplied by metrohm (herisau,Switzerland)coupled with E 506 polarocard and E 612 VA scanner. Cyclic voltamograms obtained by adigital electroniocs model 2000x-y/t recorder (Mumbai,India) in cnection with the above unit. The DME used had an area of 0.223cm^2 at adrop time of 2s. A hanging mercury drop electrode (HMDE) used had an area of 0.223cm^{2}in cyclic voltammetry. In all the above experiments platinum wire was used as auxillery electrodeallthe experiments were performed at 25^{0}C. P^H mesurements were carried out with elico digital pH meter (Hyderabad, India). The millicoulometric apparatus used was supplied by radelkis (Budapest,hungary) cotrolled potential eklectrolysis was carried out using a techno potentiostat (tech.ini electronics, luknow, India) in amidified cell with a mercury pool cathode saturarted colomel reference electrode.

Reagents and solutions

Pure samples obtained from rallis india limited. The purity of sample was tested with tin layer chromatography and melting point determinations. A stock solution of pesticides under investigation were prepared in dimethylformamide. Universal buffer cotaining 0.2 Mboric acid, 0.05Mcitric acid and 0.1M trisodium orthophosphate were used as supporting electrolyte.

RESULT AND DISCUSSION

The electrochemical reduction of valone was studied in universal buffer and consisted of a single step process in the pH range 2.0-6.0. The effect of pH on the polarogram have been investigated by recording the current voltage curves of valone at concentration of 1.0x10^{-5}M. For experimental results obtained by CV and DPP,the facile simultaneous reduction of 3carbonyl groups in valone in the present study found to proceed with asix electron addition. Typical voltammograms are shown in Figures 1-2.

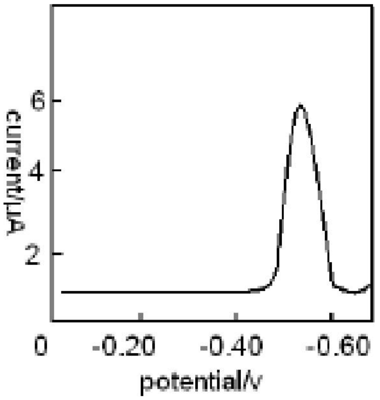


Figure 1 : Differential pulse polarogram of valone at pH 4.0 concentration:1.0 x 10^{-5}M; pulse amplitude: 50 mV droptime: 2sec.

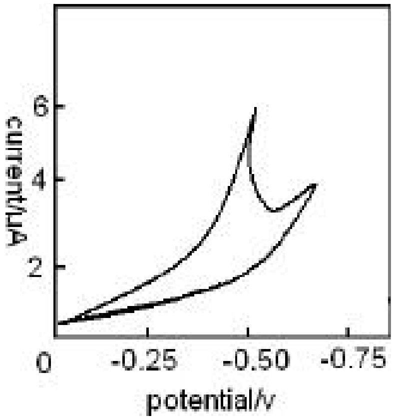


Figure 2 : Typical cyclic voltammogram of valone for an accumulation time of 80 sec at HMDE, accumulation potential: -0.6V; Rest time: 10 sec; stirring rate: 1500 rpm; scan rate: 45 mV s^{-1}; concentration: 1.0x10^{-5} M; pH:4.0.

Figure 1 exhibits differential pulse polarogram for 1 x 10^{-5}M valone with DME. The systematic studies of the various experimental and instrumental parameters that affect the polarograms response were carried out in order to establish the optimum conditions. Typical cyclic voltammogram are shown in Figure 2. No reduction peak is observed in basic medium ($8 \leq pH \leq 12$) for carbonyl groups due to the precipitation of electroactive species.

The diffusion controlled nature of the electrode process is evidenced from the linear plots of i_p vs $v^{1/2}$ and that pass through the origin indicating the adorption on electrode surface in all pHs. The experimental constancy of $i_p/v^{1/2}$ with scan rate (V) has shown the electrode process to be free from any kinetic complications. Conventional log-plot analysis and the variations of E_p values towards more negative potentials upon increasing the concentration of valone indicated the irreversibility of electrode process

Effect of pH

The pH of a solution is critical factor affecting both the rate and equilibrium state of the reduction process and the rate of the electrode reaction. The influence of the pH on the DPP response was studied at DME of the 1×10^{-5} M Valone between the pH ranges 2.0 to 6.0. It can be observed from Figure 3 that the maximum peak currents are obtained with pH 4.0.

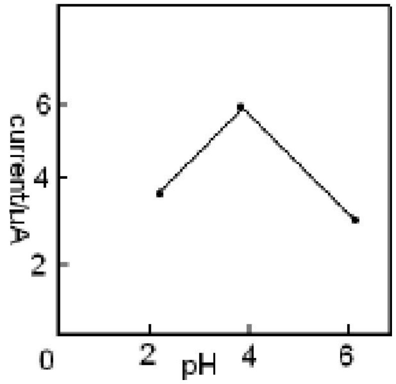
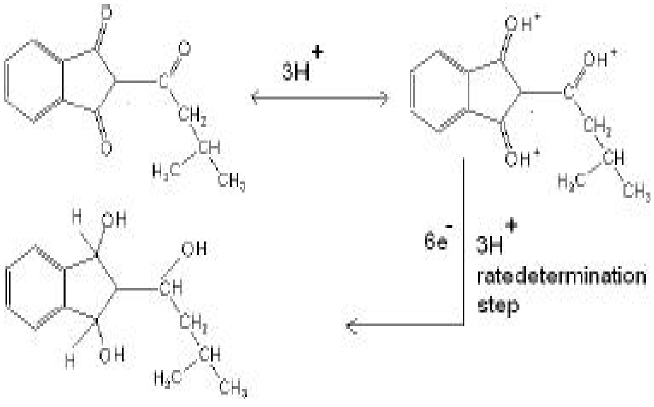


Figure 3 : Effect ofpH on peak current of valone



Scheme 1 : Electrode mechanism of valone

Electrode mechanism On the basis of the results obtained as well as from the literature, the reduction mechanism as per Scheme 1 for valone was proposed at pH 4.

Analysis

Well resolvable and reproducible peak obtained for valone is useful for the analysis of valone in spiked water samples. The optimum pH to get well defined peak for the detection is found to be 4.0. The peak current is found to vary linearly with the concentration of the pesticide over the range 1.0×10^{-3}M to 1.0×10^{-5}M. The lower detection was limit found to be 1.0×10^{-5}M.

Recovery experiments

Recommended analytical procedure

A stock solution (1.0×10^{-3} M) of valone is prepared in DMF. In voltammetric cell, 1 mL of standard solution of valone is taken and 9 mL of the supporting electrolyte (pH 4.0) is added to it. Then the solution is deaerated with nitrogen gas for 10 min. after obtaining the polarograms, small additions of standard solution are added and the pollerograms are recorded under similar experimental conditions.

Determination of valone in spiked water samples

Water samples, were collected form swarnamukhi river belt,Vakadu, Nellore district, A.P., India. These samples were filtered through a Whatman No.41 filter paper and known amount of valone were added. Aliquots of water samples were taken in a 25mL graduated tube, to it buffer solution was added and analysed as described above. The recoveries of valone obtained in both water smples ranged from 92.50 to 98.16% and the results are summarized in TABLE 1.

TABLE 1 : Recoveries of Valone in spiked water samples

Sample	Amount added (µg/mL)	Amount found (µg/mL)	Recovery (%)	Standard deviation
Tap water	2	1.85	92.5	0.018
	4	3.76	94.0	0.016
	6	5.79	96.5	0.015
River water	2	1.90	95.0	0.042
	4	3.85	96.5	0.011
	6	5.89	98.16	0.028

CONCLUSION

The method shows a good reproducibility and high accuracy compared with spectrophotometric, spectrofluorimetric and chromatographic methods of analysis.

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