

VOLTAMMETRIC STUDIES OF ANTHRAQUINONE-BASED CHLOROTRIAZINE REACTIVE DYES ADSORBED AT MERCURY ELECTRODE

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INTRODUCTION

Dyes with a suitable group capable of forming a covalent bond with the substrate are called reactive dyes. Anthraquinone-based chlorotriazine reactive dyes are being widely used in dyeing cellulose, cotton and wool (1). During alkaline dyeing an hydrolysis of this type of dyes occurs limiting the efficiency of dyeing to about 70-80%. As these dyes and their hydrolysis products can become an environmental problem, it is important their monitoring in dyebaths and in wastewater.

A procedure based in cathodic stripping voltammetry with adsorptive accumulation for the determination of the anthraquinone-based chlorotriazine reactive dyes Procion Blue MX-R and Cibacron Blue 3GA has been suggested in a previous work (2). Two voltammetric peaks were obtained, due to the reduction of the anthraquinone moiety and of the chlorotriazine moiety of the dye, respectively. The small voltammetric signal observed for the first reduction process was interpreted by Fogg *et al* (2), assuming that the reduction of the adsorbed species is very fast and reversible. With a more versatile equipment it was possible to study the effect of current sampling time on the peak current.

In order to try to modify the rate of the electrochemical reactions at the electrode, two approaches were tested: the effect of adding surfactants and the influence of electrolyte concentration. A change of the results in the presence of surfactants was observed, probably due to modification on the surface adsorption of the dyes. Results were also affected by the electrolyte concentration, a situation that can be explained as a consequence of changing the resistance of the solution.

Finally, some results for the interaction of boric acid with Procion Blue MX-R are presented and the possibility of simultaneous determination of the reactive dye and its hydrolysed form is considered.

EXPERIMENTAL

Voltammetric work was performed using an Autolab PSTAT10 voltammetric system (Eco Chemie) controlled by a PC equipped with a GPES for Windows-version 4.2 software. An important parameter to be controlled, in this work, is current sampling time. With this equipment, for pulse periods longer than 40 ms, the sampling time of differential pulse and square wave techniques is 20 ms. For shorter pulse periods, the current sampling time is half of the pulse period. A Metrohm 663 VA voltammetric stand was used in its static mercury drop electrode mode (SMDE) with a glassy carbon auxiliary electrode and a Ag/AgCl (in 3 M KCl) reference electrode.

Samples of Procion Blue MX-R and Cibacron Blue 3GA were from Merck Ltd.

Solutions were deoxygenated by passing nitrogen during 10 minutes. Stirring was switched on during adsorptive accumulation, and switched off five seconds before initiating the stripping scan, allowing the solution to become quiescent.

RESULTS AND DISCUSSION

Enhancement of the adsorptive stripping signal of the anthraquinone group

In processes involving adsorption, species are immediately available for reaction at the electrode, in opposition to diffusion controlled processes where species need to diffuse from the bulk of the solution. So, if current sampling is taken earlier after pulse application, a much higher signal can be obtained with adsorptive accumulation, provided

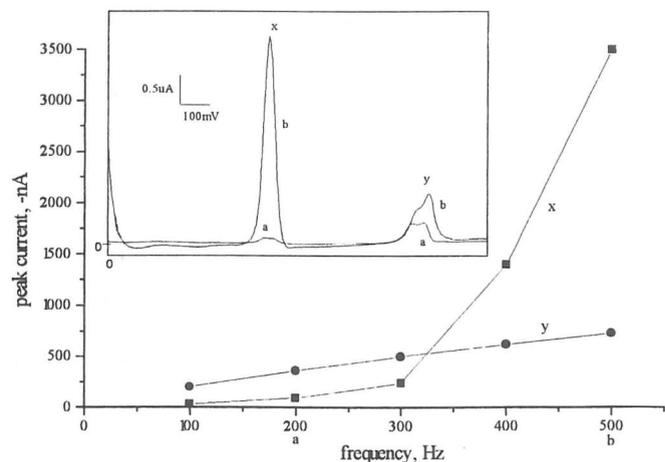


FIG. 1 - Effect of frequency on the square wave reduction peaks of (x) anthraquinone group and (y) chlorotriazine group, for a 5×10^{-7} M Procion Blue MX-R solution (0.1M acetate buffer). Box: SW voltammograms at two frequencies: a) 200Hz and b) 500Hz. SW amplitude, 20mV; step potential, 2mV; 1 min. accum. at initial potential. 0V.

that sampling is only made after the capacitive current becomes negligibly small(3).

Figure 1 shows the effect of frequency on the reduction peaks of Procion Blue MX-R (5×10^{-7} M) in acetate buffer solution (0.1M, pH 5). For the first peak (≈ -530 mV), corresponding to the reduction of the anthraquinone group, current intensity has a sudden increase for frequencies >300 Hz, probably because all the adsorbed species is reduced very fast. Komorsky-Lovric and Lovric (3) have stated that, for very fast and reversible reactions in which both reactant and product are adsorbed at the electrode surface, the adsorptive currents will disappear very quickly.

The second peak, corresponding to the reduction of chlorotriazine group, has a much lower dependence on current sampling time.

Generally, it is accepted that there is a competition between surfactant and analyte for adsorption sites at the electrode surface, which explains the decrease in voltammetric signal in presence of surfactants (4, 5). Nevertheless, there are cases of enhanced sensitivity due to their presence (6). The fact can be explained assuming that, in the presence of the surfactant, the rate constant of the electrochemical reaction decreases, causing a delay in the reduction process. This effect was observed for the reduction of the anthraquinone group of Procion Blue MX-R, as it can be seen in Figure 2. It is clear that much higher values of peak current are obtained for frequencies below 400 Hz, proportioning an increased sensitivity, if enough Triton X-100 is present (7).

Another possibility to increase the adsorptive stripping signal is by decreasing the electrolyte concentration (8). The square wave voltammetric results obtained with Procion Blue MX-R for different acetate buffer concentrations using several current

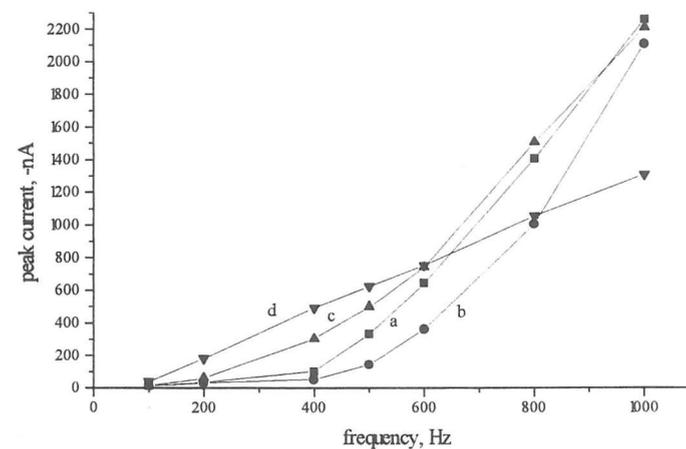


FIG. 2 - Effect of Triton X-100 on the SW reduction peak of the anthraquinone group for a 1×10^{-7} M Procion Blue MX-R solution (0.1M acetate buffer). Triton X-100 concentration (mg/L): a) 0; b) 1; c) 2.5; d) 5; other experimental conditions as in Fig. 1.

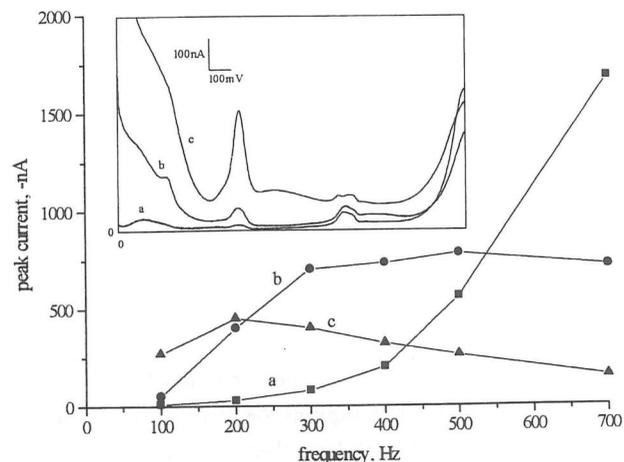


FIG. 3 - Influence of the electrolyte concentration (pH 5 acetate buffer) on the SW reduction peak of the anthraquinone group, for a 1×10^{-7} M Procion Blue MX-R solution. Electrolyte concentration: a) 0.05M; b) 0.01M and c) 0.004M. Box: SW voltammograms for a frequency of 100Hz; other experimental conditions as in Fig. 1.

sampling times are shown in Figure 3. As we can see, maximum peak currents are moved to lower frequencies (higher current sampling times) if electrolyte concentration is diminished. The simultaneous effect of electrolyte concentration and Triton X-100 on the voltammetric determination of Procion Blue MX-R is shown in figure 4. It is important to notice that the capacitive current decrease in presence of Triton X-100, when low electrolyte concentration are used (voltammograms c and d).

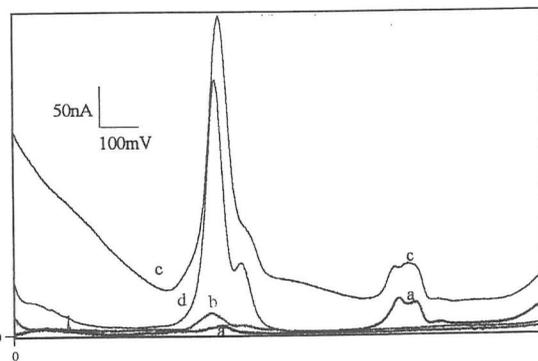


Fig. 4 - SW voltammograms illustrating the effect of electrolyte concentration and Triton X-100, simultaneously, on the determination of Procion Blue MX-R, 2×10^{-7} M. a) and b) in acetate buffer 0.1M; c) and d) in acetate buffer 0.01M; a) and c) without; b) and d) with Triton X-100, 2.5mg/L. Frequency, 100 Hz.

Interaction between Procion Blue MX-R and boric acid

Boric acid is known to complex with several anthraquinone type compounds and to alter the voltammograms obtained due to complex formation (9). Making a single cyclic scan with different rates, Fogg *et al* (2) have noticed a shift of the cathodic peak potential in the negative direction, by an amount that approaches 31mV per 10-fold increase in scan rate. Based on that they concluded that the process included a chemical reaction following charge transfer.

With multiple scans, cyclic voltammograms show that, in acetate buffer (0.1M, pH 5), a reversible redox process involving the complex formed between a product of the reduction of Procion Blue MX-R with boric acid, must exist (peaks a1 and c1 of fig.5B). In fact, for the first scan we did not observe peak c1, because at that potential there is no reduced anthraquinone form yet. Another observation from fig. 5 is that the wave at -1.17mV, corresponding to reduction of chlorotriazine group, disappears after the first scan, probably because this group is no more present at the electrode surface.

Taking into account that with sodium dithionite it is possible to reduce 1-hydroxy-9,10-anthraquinone to 1-hydroxy-9,10-anthrahydroquinone (9), we decided to add sodium dithionite to a solution of Procion Blue MX-R solution and boric acid in order to verify if the peak a1 is due to the oxidation of an eventual complex anthrahydroquinone-boric acid. Scanning the potential from -0.4V to 0 V, we did not observed the appearance of that peak either with or without sodium dithionite. This seems to prove that peak a1 is not due to the oxidation of an eventual complex formed between the anthrahydroquinone form of Procion Blue MX-R and boric acid.

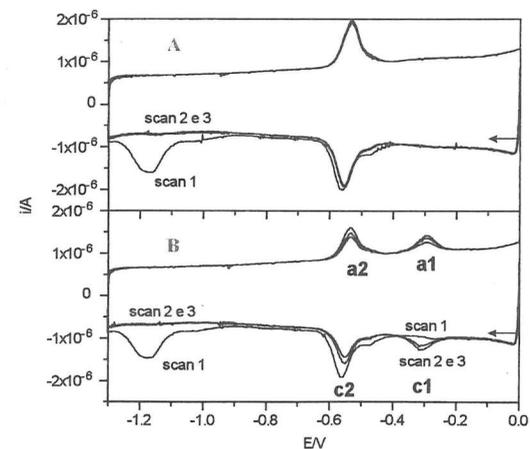


Fig. 5 - Cyclic voltammograms of Procion Blue MX-R 5×10^{-7} M in acetate buffer 0.1M: A) without; B) with boric acid 0.009M; 1V/s; $E_{mi}=E_{acc}=0V$ (30s); $E_{step}=2mV$.

Alkaline hydrolysis of Procion Blue MX-R

Investigation of the hydrolysis of the reactive dyes was carried out by heating at 80°C, for 120 minutes, 10 mL of Procion Blue MX-R solution in NaHO 0.1M. After cooling and neutralization with HCl 1M, samples were diluted to 25 mL with acetate buffer 0.1M, pH 5. In figure 6 we can see the voltammograms obtained for a standard solution of Procion Blue MX-R, prepared by the same procedure, but without submission to hydrolysis (voltammogram 1) and for the hydrolysed solution (voltammogram 2). The loss of chlorotriazine peak and the appearance of a new peak, not yet characterised, for the hydrolysed solution can be important to monitor hydrolysis product in presence of these dyes.

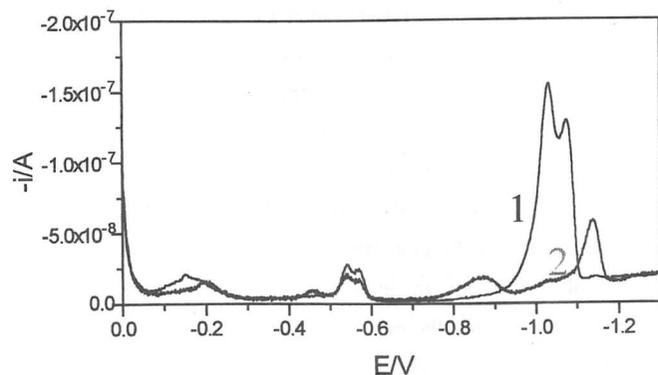


Fig. 6 - SW voltammograms obtained in the following situations: 1) for a standard solution of Procion Blue MX-R, 4×10^{-7} M; 2) for the hydrolysis solution (final conc. 4×10^{-7} M); Frequency, 100 Hz. Other conditions identical to fig. 1.

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ELECTROANALYTICAL DETERMINATION OF MOLINATE

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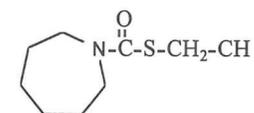
Abstract

The electrochemical oxidation of molinate, a thiocarbamate herbicide, has been studied in order to determine it in a phytopharmaceutical product. A square wave voltammetry electroanalytical method has been developed and the results were in good agreement with those obtained by the AOAC reference method using gas chromatography. The recovery is 100.2%.

Keywords: Molinate, thiocarbamate, herbicides, square wave voltammetry.

Introduction

Molinate is a thiocarbamate and its electrochemical oxidation has been studied with a view to its determination in a phytopharmaceutical mixture. It is one of the most successful herbicides that has been used in the treatment of rice crops. Due to possible contamination of water basins near the land where it is applied it is very important to develop fast and inexpensive methods for its quantification. It has the following molecular structure



Several analytical methods have been developed for the determination of molinate in different samples such as spectrophotometric methods [1], gas chromatography [1-5], liquid chromatography [5, 6], thin layer chromatography [1, 7-9] and immunoassays [10, 11].

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