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Effect of Current Sampling Delay on the Sensitivity of Adsorption Voltammetry

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Introduction

Accumulation of species at electrodes is a very well known process of increasing the sensitivity of voltammetric methods[1]. After the accumulation step, species are voltammetrically stripped, usually by application of a pulse technique, as differential pulse voltammetry (DPV) or square wave voltammetry (SWV).

Anodic stripping voltammetry (ASV) using a hanging mercury drop electrode (HMDE) is the more popular example of this type of methods, specially used for the determination of several metal ions: on a first step, a sufficiently cathodic potential is applied to reduce the metal ion to metal, which accumulates at the drop as an amalgam; on a second step, an anodic scan is applied to the drop and the metal is stripped by reoxidation. It is this reoxidation anodic current that is measured and related with the metal ion concentration in the solution. In a similar way, cathodic stripping voltammetry (CSV) can be used in the determination of species that are accumulated in the sequence of an oxidation and then stripped during a cathodic scan.

A third voltammetric process involving an accumulation step is adsorption voltammetry, which can be used in the determination of species that adsorb at the surface of the electrode[2]. During the accumulation step (usually non-faradaic) the concentration of the species increases at the electrode surface by adsorption; after accumulation, a potential scan is applied to the electrode and the faradaic current resulting from the stripping of the species is measured. In some cases the current measured results from a non-faradaic desorption caused by the potential scan, a process that is called tensammetry.

In this work it will be shown that the sensitivity of adsorption voltammetry can be greatly enhanced if current sampling is taken earlier after the potential pulse application. Also, taking into consideration that normal pulse voltammetry (NPV) is a well established technique for the characterization of adsorption effects at electrodes[3], it will be shown that the current sampling delay after pulse application has an important influence on the detection of those effects. Finally, the influence of the presence of surfactants on adsorption voltammetry is considered, with discussion of a situation where the relative effect of surfactant concentration on current peaks varies with the current sampling time.

Experimental

Voltammetric work was performed using an Autolab PSTAT10 voltammetric system (Eco Chemie), controlled with a PC equipped with a GPES for Windows - version 4.2 software. A Metrohm 663 VA voltammetric stand was used in its hanging mercury drop electrode mode (HMDE). A glassy carbon auxiliary electrode and a AgCl/Ag (in 3 M KCl)

reference electrode completed the three electrode potentiostatic system.

Before the adsorption period, solutions in voltammetric cell were deoxygenated by passing nitrogen during 10 minutes. Stirring was switched on during the adsorption period, and switched off ten seconds before initiating the stripping scan.

Frequency and Sensitivity in Adsorption Voltammetry

One important difference between processes controlled by diffusion and processes involving adsorption is that in this last case species are immediately available for reaction at the electrode, as they do not need to diffuse from the bulk of the solution; this means that i_{ads} has a much faster decay with time (pseudo - capacitive) than i_{dif}[4,5,6]. As we can see in Figure 1, if current sampling is taken earlier after pulse application a much higher increase in sensitivity is obtained with adsorption methods than with diffusion methods, as soon as sampling is only initiated after i_{cap} becomes negligibly small.
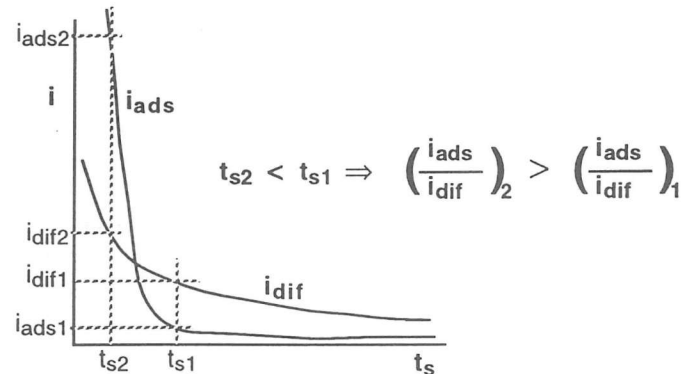

$$t_{s2} < t_{s1} \Rightarrow \left(\frac{i_{ads}}{i_{dif}}\right)_2 > \left(\frac{i_{ads}}{i_{dif}}\right)_1$$

Figure 1. For very short sampling times (t_s) the increase in i_{ads} is much higher than the increase in i_{dif}.

This effect can be confirmed in Figure 2, representing DP voltammograms for the analysis of the colouring matter carmoisine using a HMDE and 60 seconds of accumulation. The large increase in the reduction current for shorter pulse times indicates that the colouring matter is adsorbed at the electrode surface. But there is another important advantage in using shorter sampling times: it is possible to use much higher frequencies in DPV if we reduce the pre-pulse time and, in consequence, much fast scanning rates can be obtained, which allowed a drastic reduction of the analysis time.

It is worthy to note that SWV is very similar to DPV if we consider this last technique with equal pre-pulse and pulse times; in this case the only difference is that the pulse superimposed to the potential ramp oscillates between 0 and $-\Delta E$ in DPV and between $+\Delta E/2$ and $-\Delta E/2$ in SWV[7].

It is important to point out, also, that there is another reason for the increase in sensitivity obtained with high frequency DPV and SWV methods: as the species formed at the electrode have no time to diffuse before the following pulse they can be reduced and reoxidized more than one time in the electrochemical reactions at the electrode, with a

consequent increase in the measured current (effect predictably more pronounced in reversible processes)[7].
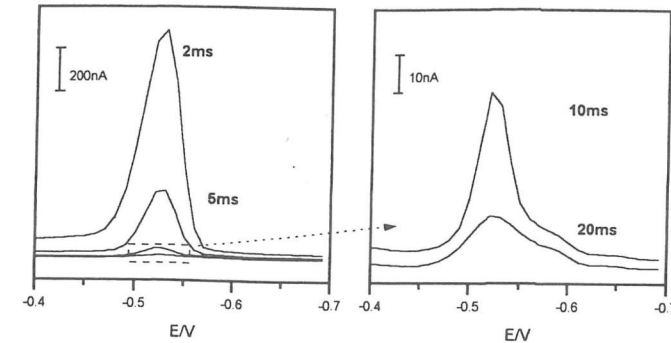

Figure 2. DP voltammetric analysis of 10^{-7} M carmoisine in ammonia buffer (pH=9), using different pulse times: 2ms, 5 ms, 10 ms and 20 ms. Other voltammetric conditions: accumulation at -400mV for 60s; pulse interval=1s; scan rate=5mV/s; and pulse amplitude=-50mV.

Normal Pulse Voltammetry (NPV) in the Detection of Adsorption

NPV is an appropriate technique to find out if adsorption is present. In fact adsorption is identified by a large peak superimposed on the sigmoidal shaped NP voltammogram (Figure 3). This peak appears near the half wave potential, where the decrease of the adsorption current with time is not so fast[3].
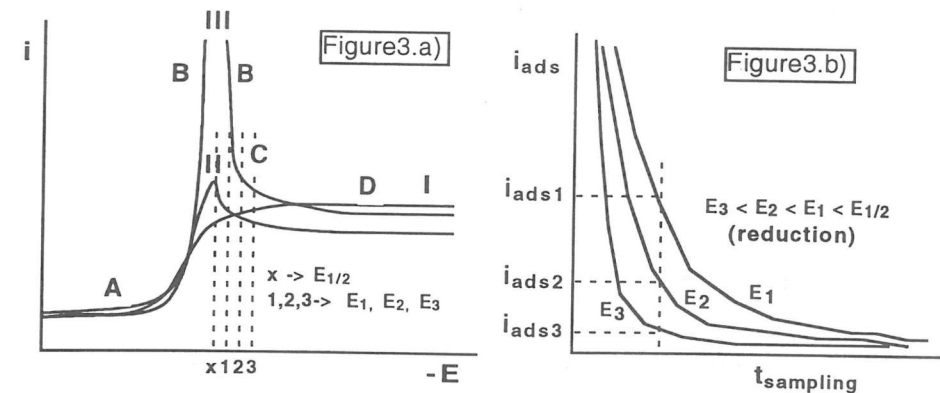

Figure 3. NPV in the identification of adsorption. I - no adsorption (normal case, only with diffusion); II - weak adsorption (near $E_{1/2}$, i_{ads} is slightly higher than i_{dif}); III - strong adsorption (near $E_{1/2}$, i_{ads} is considerably higher than i_{dif}). A - E >> $E_{1/2}$: no reduction; B - E $\approx$ $E_{1/2}$: reduction starts (i_{ads} > i_{dif}); C - E < $E_{1/2}$: i_{ads} starts to disappear at the sampling time (Figure 3.b)); D - E << $E_{1/2}$: i_{ads} practically disappears (Figure 3b)) and only i_{dif} is measured.

In Figure 4 we can see normal pulse voltammograms of one adsorbing and one non-adsorbing species, respectively dimethylquinoxaline (DMQ) and cadmium (II) cation, using several pulse times in each case. In the case of the cadmium (II) ion the well known sigmoidal shape of NP diffusion voltammograms is obtained at all pulse times, indicating that the metal ion is not adsorbed. For DMQ, this situation only happens for the higher pulse time (50 ms), because in this case the adsorption current is almost vanished; if pulse time is shortened adsorption current increases much faster than diffusion current and this last becomes almost negligible (see Figure 1). As a consequence adsorptive peaks can be observed for DMQ , increasing with decreasing pulse time.
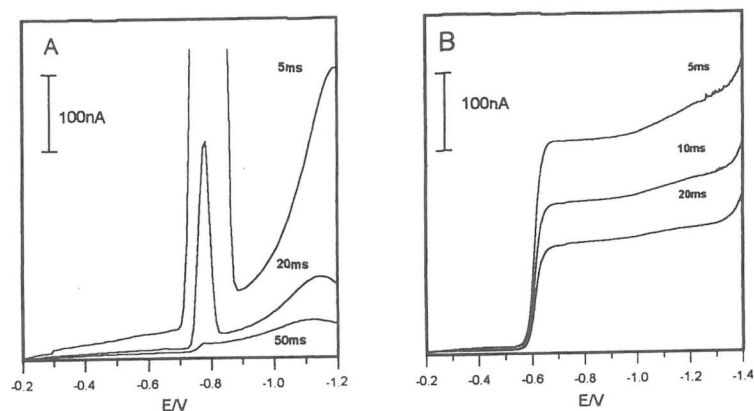

Figure 4. Effect of pulse time on the NP voltammetric analysis of: A - DMQ 1x10-6M; B - cadmium (II) 1,5x10-5M. Other voltammetric conditions: accumulation at -200mV for 30s; pulse interval=1s; step potential=5mV/s; and base potential =-200mV

Effect of Surfactants on Adsorption Voltammetry

It is well known that adsorption voltammetry is affected by the presence of surfactants; the usual explanation for this is based on the competition of the surfactants with the analytes for the adsorption positions at the surface of the mercury electrode[8]. Nevertheless, there are situations (which fall outside that explanation) where the addition of surfactants enhances the signals obtained, allowing an increase in sensitivity[8].

In earlier studies[8] the addition of TPPC was found to increase the sensitivity of carmoisine analysis; in order to understand this unexpected effect it was decided to perform similar studies using different pulse times. The results obtained in these experiments suggest that, in fact, the effect of this surfactant is not as simple as a competition for the adsorption sites (Figures 5 and 6). It seems that TPPC has an overall slowing effect on the rate of the electronic transfer at the electrode, and so the relative signals with and without TPPC are dependent on the sampling time. This conclusion is in good agreement with the behaviour predicted by Komorsky-Lovric and Lovric, for a situation of adsorption of both the reactant and the reaction product[9].
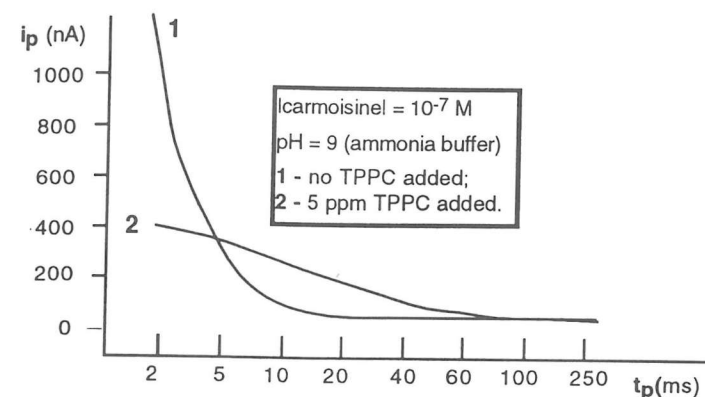

Figure 5. Effect of pulse time on the DPV determination of carmoisine, with and without TPPC. Voltammetric conditions similar to Figure 2
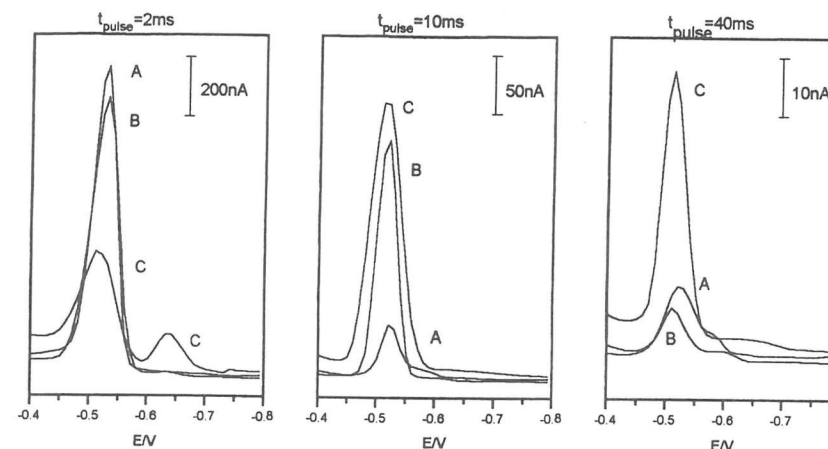

Figure 6. Effect of TPPC concentration and pulse time on the DP voltammetric signals for carmoisine. TPPC concentration (ppm.): A - 0; B -1 ; C - 5ppm. TPPC has a reduction effect on the signals only for shorter pulse times.
Voltammetric conditions: accumulation at -400mV for 60s; pulse interval=1s; scan rate =10mV/s; and potential amplitude =-50mV.

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