MONITORING REACTIVE DYES AND THEIR HYDROLYSIS AND METHANOLYSIS PRODUCTS BY CATHODIC STRIPPING VOLTAMMETRY AT A HANGING MERCURY DROP ELECTRODE

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The intention of this paper is to review the present position with regard to the use of cathodic stripping voltammetry (CSV) with reactive dyes. This work is part of a wider study in these laboratories on the determination of a diverse range of organic determinands using CSV. Most of this work - including all that on the reactive dyes - has been carried out with an unmodified hanging mercury drop electrode (HMDE), although other CSV studies have been made using a poly-L-lysine modified HMDE and this has been extended to the use of screen-printed carbon electrodes.[1]

Stripping voltammetry (SV) using an HMDE is a simple, relatively inexpensive technique. It is important to use a modern, reliable, commercial HMDE unit: with such a unit, individual HMDEs can be produced quickly, reliably and reproducibly. The electrode assembly is completed with conventional auxiliary and reference electrodes. SV is a two-step process: accumulation for a fixed time being followed by determination using a suitable voltammetric waveform (linear sweep, differential pulse, square wave, etc).

Adsorptive accumulation was known to increase the sensitivity of differential pulse polarographic measurements owing to accumulation of the determinand between pulses (see *e.g.* Barker and Bolzan[2], Rooney[3]). The first analytical use of adsorptive accumulation with the HMDE appears to have been made by Nurnberg and co-workers in 1980/1 in determining Ni with added DMG.[4,5] Kalvoda[6] published a paper on adsorptive accumulation in stripping voltammetry in 1982: the adsorbed organics were determined tensammetrically, *i.e.*, by desorption. The term adsorptive stripping voltammetry seems to have been first used by Lam, Kalvoda and Kopanica[7] in 1983 in the paper *determination of uranium by adsorptive stripping analysis*. In 1984 Kalvoda[8]

Portugaliæ Electrochimica Acta, 14 (1996) 229-232

extended this in his paper *adsorptive stripping voltammetry of electroactive organic compounds*. The new technique was developed rapidly by van den Berg with seven papers in 1984 involving adsorption of metal complexes of copper, uranium, vanadium, zinc, and iron in seawater,[9] and by Wang in 1985 with eight papers involving adsorption of metal complexes and organics.[9] Further information on methods of accumulation and stripping in SV can be found in papers by the present author.[9,10]

Dyes are grouped according to their chromophores (*e.g.* anthraquinone, azo, etc) or the method of dyeing used (*e.g.* acid, disperse, mordant, reactive, etc.). The chromophore in reactive dyes is commonly the azo or anthraquinone group. Reactive dyes are unique in reacting and forming covalent bonds with the textile fibre. There are numerous types of reactive groups, but the main ones used are the chlorotriazine and sulfatoethylsulfone groups: in the case of the latter group sulfate is first eliminated giving the vinylsulfone group which reacts with the textile. Hydrochloric acid is eliminated in the reaction of chlorotriazines with the hydroxyl group of cotton, whereas the vinylsulfone group adds directly to the hydroxyl group.

Procion Blue MX-R and Cibacron Blue 3GA are anthraquinone chlorotriazine reactive dyes. In the reactive dyeing processes only about 80 per cent of a reactive dye bonds covalently to the cotton, the other 20 per cent being hydrolysed. Our initial choice of differential pulse CSV for studying Procion Blue MX-R and Cibacron Blue 3GA11 was, in some respects, unfortunate as the differential pulse CSV signal for the reduction of the anthraquinone group is virtually absent in buffers which do not contain boric acid. This lack of a differential pulse signal was considered to be due to the very rapid reduction of this group in the adsorbed molecule which is complete before the current is measured at the end of the potential pulse. The signal is present when the linear sweep waveform is used. The differential pulse signal for this group is present for the reactive dye when borate-containing buffers, such as Britton-Robinson buffer, are used, and also for the hydrolysed reactive dye in any buffer. [Borate forms complexes with the anthraquinone moiety]. Peaks at more negative potentials are present in all acidic buffers for the reduction of the chlorotriazine group. Thus, the hydrolysis of these reactive dyes can be followed using both the disappearance of the peak due to the reactive group or

the appearance of that due to the anthraquinone group.[12] The reaction of the reactive dyes with methanol, which is used to simulate the dyeing process without the complication of the diffusion of the dye and reagents through the fabric, can be followed similarly.[12] More extensive studies have been reported on the polarography[13] and cathodic stripping voltammetry[14] of these two dyes.

Taylor and Renfrew synthesised a series of azo reactive dyes containing a triazine ring with different leaving groups attached.[15,16] These were used by Taylor and Renfrew in HPLC studies to compare the effect of the leaving group on the proportion of each dye reacting with methanol as opposed to being hydrolysed. The polarography and voltammetry of these dyes were studied by us.[17,18] Peaks due to the reactive groups were observed for the dyes containing the following groups on the triazine ring: chloro-SCH_2CH_2OH,[17] 4-carboxypyridyl, and DABCO.[18] The hydrolysis of these dyes could be followed using the decrease in size of these peaks, and in the case of the 4-carboxypyridyl compound by the appearance of the polarographic peak of 4-carboxypyridine.

Reactive Violet 5 is the copper complex of an *o,o'*-dihydroxy azo dye which also contains the sulfatoethylsulfone reactive group. Peaks are obtained for reduction of the complexed copper and for reduction of the azo group for both the reactive dye and for its hydrolysed product.[19] The copper peaks can be eliminated by using a pH 6 EDTA buffer, and, as the azo peaks of the reactive and hydrolysed dyes are sufficienly separated, the hydrolysis can be monitored by observing the decrease of the azo peak of the reactive dye and the growth of the azo peak of the hydrolysed dye. Reactive Violet 4 behaves similarly.[20]

Current work on reactive dyes in these laboratories includes an assessment of CSV for monitoring reactive dye and hydrolysed dye in 'spent' dyebaths and washes. Studies are also being made of reactive dyes with dichloroquinoxaline and dichlorophthalazine groups. These studies will be reported shortly.

Acknowledgements

The authors thank other colleagues involved in these studies, *viz.* J.Barek, J.Zima (Charles University, Prague), R.Ahmad, R.Yusoff (Technical University of Malaysia), and A.Ion (Technical University, Bucharest).

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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)