ELECTROPOLYMERIZATION OF VITAMIN B_{12} DERIVATIVES

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Abstract

The electrochemical behaviour of Vitamin B_{12} derivatives with cobalt (III) complex and containing an alkyl chain with a peripherical pyrrole group is analysed by cyclic voltammetry. Adsorption of the derivatives under oxidised and reduced forms appears to allow the oxidation of the pyrrole group with concomitant polymer film formation. The length of the alkyl chain has been seen to play an important role on the polymer properties namely on its conductivity and thus on the possibility of thickening the film. Although a relatively high potential is required for the adequate monomer oxidation the electropolymerization of these new monomers can be envisaged for modified electrodes preparation.

Key Words

Vitamin B_{12} derivatives; peripherical pyrrole group; electropolymerization; modified electrodes.

Introduction

In the last decades the surface modified electrodes (SME) have been subject of much research with the aim of getting better process selectivity and / or to carry out new electrochemical reactions [1,2].

Modified electrodes have been obtained by the immobilisation of catalysts reactions [3] or other molecules using different approaches including polymerization. For electrocatalysis or organic electrosynthesis the use of a polymeric matrix, namely conductive organic polymers, have shown to be quite interesting [4].

The chemical and electrochemical properties of surface immobilised transition metal complexes are of great interest [5,6] and the electropolymerization of adequate designed monomers, *e.g.* containing pyrrole substituted transition metal complexes, has been reported and widely developed due to the possibility of using modified electrodes in electroassisted catalysis [7,8].

Vitamin B_{12} is known to be electrochemically active [9,10] and, when just adsorbed on graphite, presents electrocatalytic properties for the oxidation [11] and reduction [12] of several systems, including compounds with biological interest [13].

Vitamin B_{12} derivatives containing a pyrrole group in a peripheral alkyl chain have been synthesized and, in this work, we report the results of our investigation on the electropolymerization of these large molecules.

Experimental

Pyrrole containing vitamin B_{12} derivatives with the Co complex in different oxidation states and with alkyl chains of various length - Fig. 1 - were synthesised as reported elsewhere [14].

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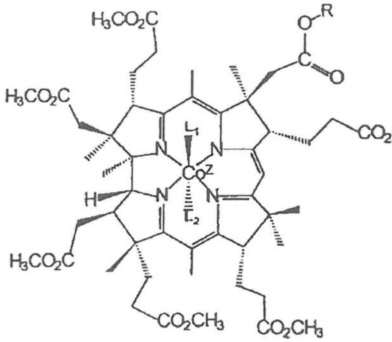

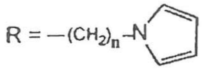

n = 3, 6, 12

Co^z	L_1	L_2	n=	3	6
Co(III)	CN	CN		d.3	d.5
		H_2O, ClO_4^-			
Co(II)	ClO_4^-	-			

Fig. 1 - Structure of the synthesised Vitamin B_{12} derivatives; d3 and d5 have been used in this work.

Monomers containing Co(III) coordinated by two cyano groups and the alkyl chain with 3 and 6 members thereafter named, respectively, as derivatives 3 and 5 have been studied .

Solutions of 0.2 mmol dm^{-3} of the synthesised vitamin derivatives have been prepared from acetonitrile (Merck, Uvasol spectroscopy grade) distilled under argon atmosphere and 0.1 mol dm^{-3} $LiClO_4$ (Riedel-de Haën) dried in a oven at 110°C for at least 24h prior to use. They were thoroughly deoxygenated directly in the cell with argon (purity > 99.9997%) before the measurements.

Cyclic voltammetry, at a vitreous carbon electrode, in a conventional three electrode cell, has been performed at a sweep rate of 150 mV s^{-1}. The electrode potentials were controlled with respect to a saturated calomel electrode (SCE) by an EG&G PAR model 273 potentiostat. A Pt foil was used as counter electrode. Prior the experiments the working electrode has been mechanically polished to a mirror finishing with successively finer grades of alumina (down to 0.05 μm), rinsed with double distilled water and with distilled acetonitrile.

Results and discussion

The current response obtained for the derivative 3, at a glassy carbon electrode, is shown in figures 1A and 1B. Starting at 0V and scanning the potential cathodically, figure 1A, a wave at about -0.9V denotes the reduction of Co(III) species; the further conversion to Co(I) appears to occur at potentials lower than -1.2V. Reversing the potential sweep, a wave at 0.13V followed by a shoulder and another broad wave at 1.55V can be observed.

When the initial potential scan is in the positive direction (figure 1B) only at E > 1.55V there is a current increase which shall correspond to the pyrrole group oxidation. Since during the subsequent cathodic sweep, besides the expected Co(III)/Co(II) and Co(II)/Co(I) reductions, there is another process taking place at -0.53V, it can be assumed that an electrode modification, likely by electropolymerization via pyrrole oxidation, occurs, being the polymer (PVB_{12}) reduced at that potential (-0.53V). It is worthwhile to point out the decrease in the current peaks associated to the metal reduction when figure 1B is compared to figure 1A, in agreement with the formation of a lower conductivity media (polymer in its reduced state).

Figure 2 displays the behaviour of the same derivative in a broader potential range and for two consecutive sweeps, starting cathodically. The extent in the derivative reduction has a well marked effect on the anodic process occurring about 1.6V, suggesting the involvement of adsorption steps. Also, in spite of the low conducting character of the phase produced during the first scan, the electropolymerization appears to proceed as denoted by the features of the second cycle (pyrrole group oxidation similar to figure 1B).

The behaviour of a similar Vitamin B_{12} derivative but with a longer alkyl chain (derivative 5) is presented in figure 3 The second cyclic voltammogram is still structured and only the third reflects the poor conductivity of PVB_{12} formed through the oxidation of the pyrrole group. This dependence of the polymeric electronic structure on the alkyl chain length might be expected considering the information obtained for substituted pyrrole monomers [15].

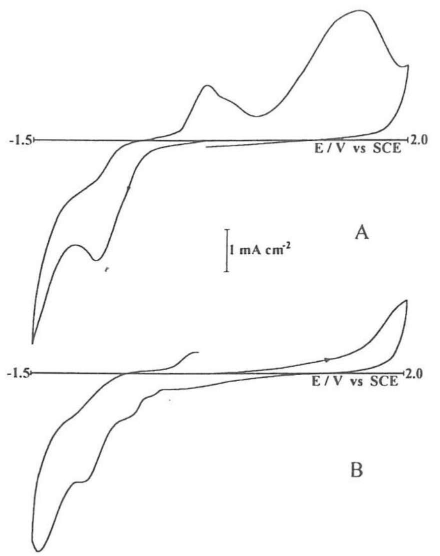

Fig. 1 - Cyclic voltammetry of derivative 3 starting the scanning cathodically (A) and anodically (B).

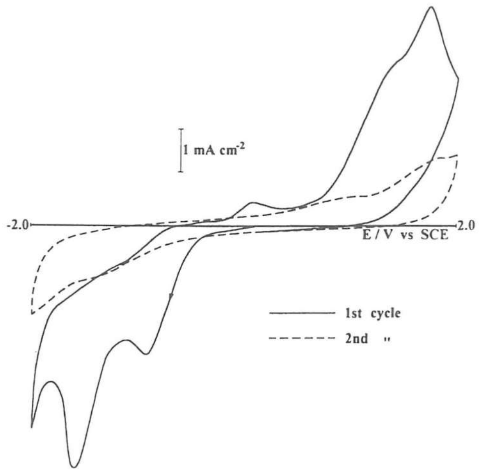

Fig. 2 - Consecutive cyclic voltammograms of derivative 3.

In figure 3, a weak anodic process at about +1V can also be noticed; as in the case of derivative 3 -figure 2 - this shall correspond to the polymer oxidation.

Using derivative 5, a set of experiments, illustrated by figure 4, were carried out within a narrower potential window. In a range where only Co(III) /Co(II) redox couple can be detected, consecutive potentials can show a remarkable decrease in both current peaks (-0.88V, +0.44V), and a potential shift of the cathodic wave to more negative potential values. These features support a

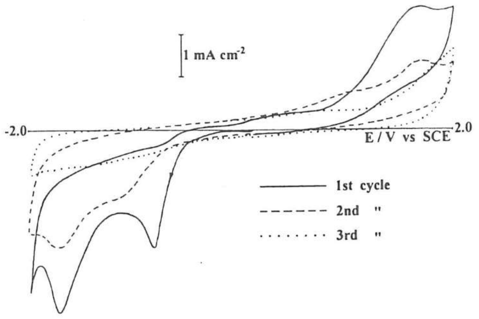

Fig. 3 - Repetitive cyclic voltammetry of derivative 5.

reaction mechanism involving the derivative adsorption, likely by the pyrrole group, which only undergoes oxidation at rather high potentials and hitherto block the electrode surface hindering the redox of solution species. Indeed, going to a further cathodic limit (until -1.5V, figure 5) the anodic counter part (+0.42V) of the first cathodic process is much smaller. It is followed by another peak at ~1V and a current increase until 1.5V. During the second and subsequent potential scans there is a dramatic decrease in the cathodic peak; on the anodic part, no peak can be defined and the current decreases as the number of cycles increases. It can also be observed in figure 5 that under continuous cycling the cathodic process is shifted cathodically and the presence of a shoulder at ~ -0.6V (second and third scans) which turns into a peak from the third scan on, denoting another reduction process.

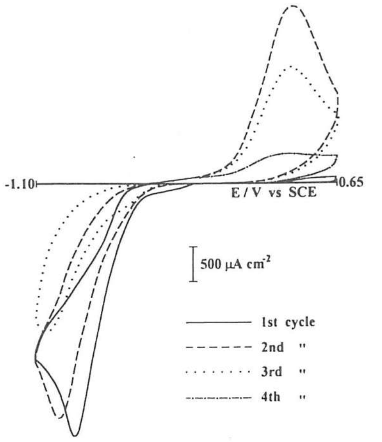

Fig. 4 - Consecutive cyclic voltammograms of derivative 5.

The mentioned voltammetric features can be interpreted by considering that both reduced and oxidised forms of the Vitamin B_{12} derivative 5 adsorb on the electrode; it is the pyrrole group in the adsorbed oxidized Co(III) form that oxidizes, at high anodic potentials, giving rise to the polymerization onset. Some Co(III) species are "consumed" in the polymer formation and thereafter the electrode area available for other adsorbed species redox conversion decreases. The shoulder at ~ -0.6V denotes the derivative 5 polymer reduction (- 0.53V for derivative 3). At the PVB_{12} modified electrodes the adsorption processes are less effective and thus lower currents are observed.

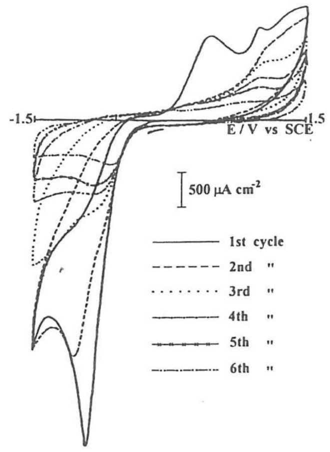

Fig. 5 -Redox behaviour of derivative 5 under continuous cycling.

Although with limited thickness, polymer films can be obtained from the derivatives considered in this work. Investigation on the influence of different metal ligands (e.g. ClO_4^-) on the electropolymerization process and on the polymer properties prepared from Vitamin B_{12} based monomers with alkyl chains of different lengths will be reported in a separate paper.

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