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# CYCLIC VOLTAMMETRIC ADSORPTION BEHAVIOUR OF RIBOFLAVIN AT PLATINUM ELECTRODE

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**ABSTRACT**

Cyclic voltammetric technique has been used to determine the electrochemical adsorption behaviour of riboflavin at platinum disc electrode in acidic solution. The electrode loses its activity after the first cyclic curve due to coating of its surface with the adsorbed species. The adsorption strength of riboflavin has been compared with some of the strongly adsorbed materials. This technique *is* employed to determine the amount of the species adsorbed on the surface of the electrode as the quantity of charge consumed is proportional to the area under the first cycle in the voltammogram.

## Introduction

Riboflavin (Vitamin $B_2$) is a well known vitamin and plays an important role in biological oxidation and reduction (Baldwin, 1967). It participates in the metabolism of proteins, carbohydrates and lipids. Riboflavin derivatives, Ravin mononucleotide (FMN) and Ravin adenine dinucleotide (FAD), are the prosthetic groups of flavoproteins which act as a member of the cellular redox system. Riboflavin, FMN and FAD possess similar redox potentials (-0.186 to -0.218 Vat pH 7) which depend largely on he 9th substituent in the molecule (Clark, 1960).

Most of the electrochemical investigations on riboflavin have been carried out in the field of polarography (Tatwawadi, 1968; Soderhyelm, 1976; Schertel, 1971; Jambor, 1965). The various aspects studied cover adsorption behaviour, semiquinone formation, half-wave potential and quantitative determination. It also appears that the electrochemical reduction of FMN in aqueous solution is complicated by the existence of protolytic equilibria between the oxidised and reduced forms of flavin semiquinone (Heais, 1982). The polarographic reduction wave of riboflavin shows a prewave indicative of the adsorption of the product of the electrode reaction (Brdicka, 1947; Kolthoff, 1957). It has been postulated that the reduction reaction occurs in approximately the same potential region where the molecules are strongly adsorbed (Ke, 1957). Another polarographic study of riboflavin indicated that pyridine eliminates the adsorption of the electroactive material (Fowler, 1952). In view of the electrochemical characteristics of riboflavin an interest was developed to study its redox behaviour by cyclic voltammetry at platinum disc electrode.

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## Materials and Methods

Riboflavin (FMN) was obtained from Sigma Chemical Company. The apparatus, instrumentation, electrode activation and its associated electronics, reagents and solution handling have been previously described (Bishop and Hussein, 1984). The voltage ramp signal was replaced by a triangular wave signal from TWG 300 Test Wave Form Generator manufactured by Feedback Ltd., England. By carefully controlling the amplitude of the triangular wave and the initial potential control, the initial and final potential of the cyclic voltammagam could be chosen. Through control of the frequency of the triangular wave use, the scan speed could be adjusted. The geometric area of the electrode was 0.503 cm'.

## Results and Discussion

### *Cyclic voltammetry of riboflavin*

The dependence of the ratio of the cathodic to the anodic peak currents as a function of scan rate is shown in Figure 1. Cyclic voltammogams of $5x10^{-3}$ $mol.1^{-1}$ riboflavin in 0.01 $mol.1^{-1}$ perchloric add showed marked difference between the rust forward sweep towards negative potential and the second subsequent cycle is identical at all scan rates. The difference between the first cathodic cycle and all the subsequent cycles prompted the conclusion that after the first cycle the electrode loses its activity due to coating of its surface with the adsorbed species. This behaviour was verified by record[i]ng the cyclic current-potential curves without pretreatment of the electrode after which the first peak disappeared (Figure le). This behaviour confirms the adsorption property of riboflavin or FMN in the electrochemical process. A similar phenomenon has also been observed for riboflavin in single scan voltammetry (Hussein and Waqar, 1992).

The cathodic and anodic peak current and potential are scan rate dependent and increase with the increase of scan *rate*, but the anodic peak increases more slowly. Changes of the width and shift of peak current to lower values with the decrease of sweep rate occur due to the increase of the adsorbed species on the surface of the electrode thus affecting its activity. The relationship of peak current against the square root of scan rate was linear with zero intercept. A plot of potential against natural log of scan rate is also linear. These plots are according to the equation formulated by Sevcik (1948) but it is not possible to interpret or to evaluate the kinetic parameters for the reduction of riboflavin due to strong adsorption of the reactant.

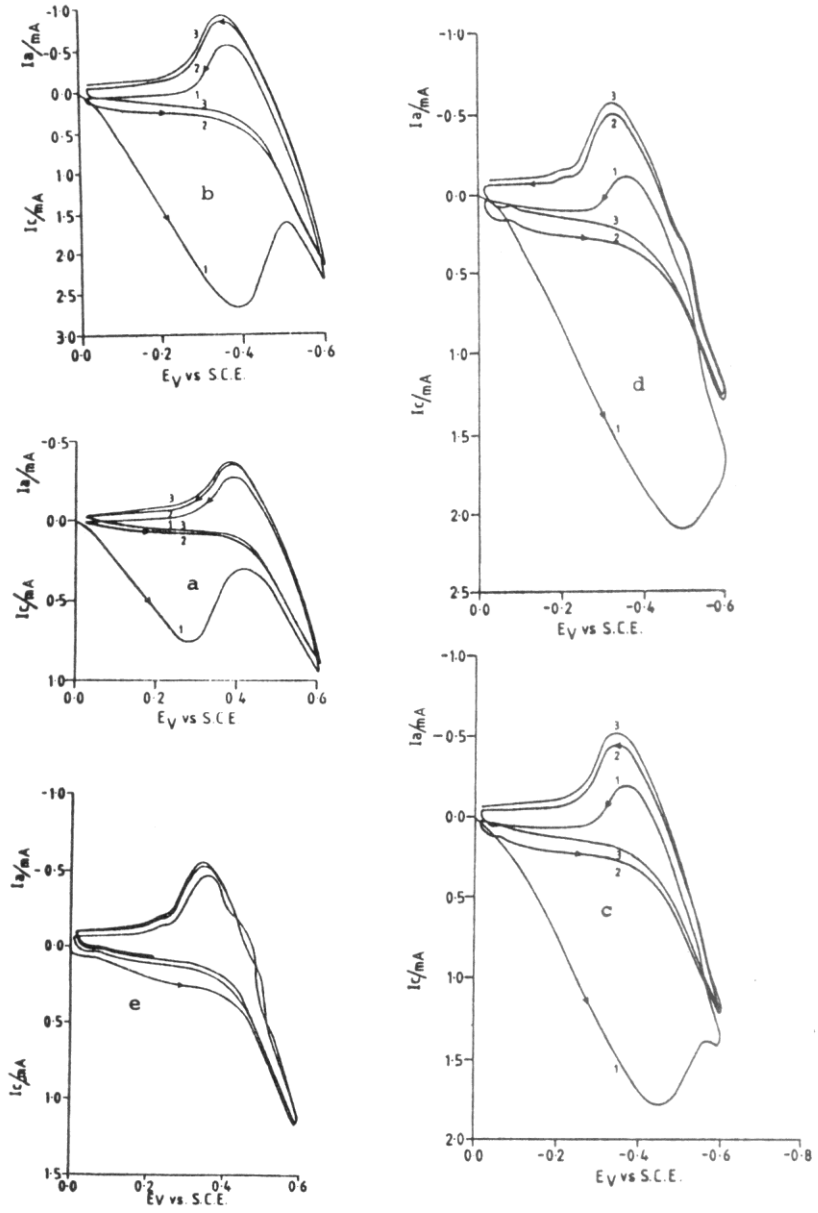


Figure 1. Cyclic voltammograms of riboflavin ($5x10^3$ $mol.1^{-1}$) in 0.01, M perchloric acid at scan rates (a) 388 (b) 100 (c) 1765 ((d) 2384 mV $s^{-1}$ at platinum electrode (area 0.503 $cm^2$); 1-3 indicates the first, second and third sweep cyclic voltanimogram of 1e recorded (without activation) just after the cyclic curve 1d at 2384 $mVs^{-1}$.

*Comparison with other adsorbents*

A comparative study of the riboflavin adsorption characteristics has been carried out with other strongly adsorbed materials (Petrii and Kotlov, 1968; Veber and Pirtakhalava, 1964; Orata, 1991). The activated platinum electrode was deactivated by being dipped in 5% potassium bromide solution for 10 seconds and was then used for recording a cyclic voltammogram. However, the same results were obtained as those before the electrode was dipped into the potassium bromide solution (Fig. 2a). The same procedure was then repeated with potassium iodide and a change in the cyclic curves was noticed (Fig. 2b). From the difference in the voltammograms with the two adsorbing agents, it appears that potassium iodide is a more powerful adsorbing agent than the potassium bromide. Nonetheless, it may, therefore, be suggested that riboflavin is a stronger adsorbing agent than either the bromide or iodide. A similar study has also appeared using pyridine (Brdicka, 1950) which resulted in the elimination of the adsorption of riboflavin. When pyridine was examined in this study, it was noticed that the reduction wave of riboflavin disappeared, being suppressed by pyridine.

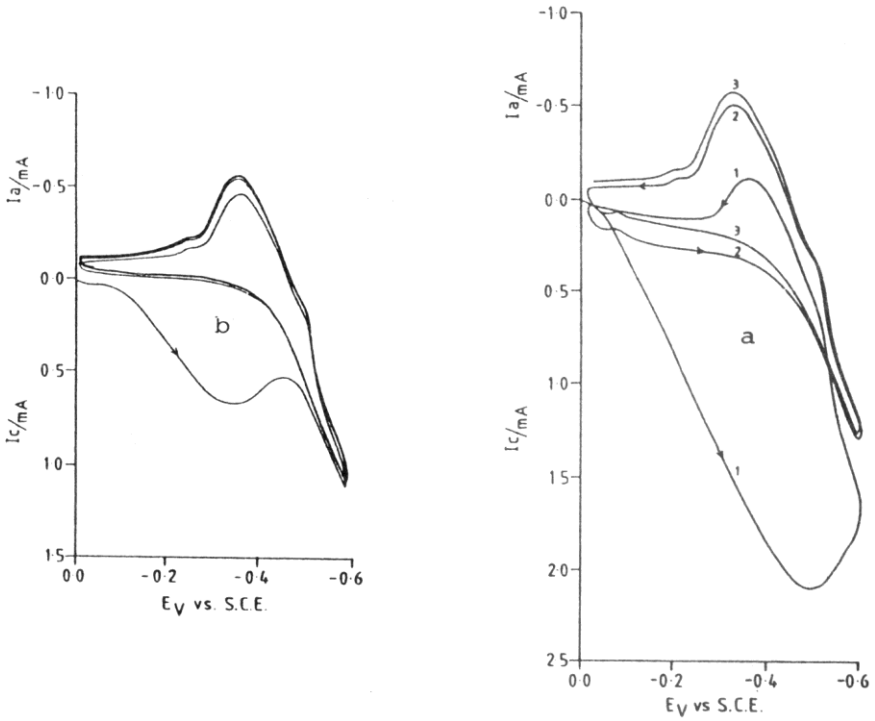


Figure 2 Cyclic voltammograms of riboflavin ($5x10^{-3}$ $mol.1^{-1}$) in 0.01M perchioric acid (a) recorded after deactivation of the platinum electrode in potassium bromide (b) recorded after deactivation of the platinum elecrode in potassium iodide, at scan rate 2384 mV $s^{-1}$, electrode area 0.503 $cm^2$.

*Evaluation of adsorbed amount*

The cyclic voltammetric technique was employed to determine the amount of the riboflavin species adsorbed on the surface of the platinum disc electrode. The area of the first cathodic half cycle was determined and is tabulated in Table 1.

**Table 1**

**Precision of determination of riboflavin adsorption on the platinum electrode (area 0.503 $cm^2$), medium 0.01M perchloric acid, temperature 25°C.**

| Scan rate $mV\ s^{-1}$ | Area of the Peak, $cm^2$ | Amount adsorbed m. coulombs |
|---|---|---|
| 200 | 0.74 | 1.233 |
| 400 | 1.14 | 1.140 |
| 588 | 1.65 | 1.100 |
| 769 | 2.52 | 1.008 |
| 1000 | 3.04 | 0.894 |
| 1365 | 3.20 | 0.800 |
| 1765 | 3.99 | 0.665 |
| 2000 | 4.33 | 0.541 |
| 2384 | 4.78 | 0.398 |

The increase of the area with the increase in the sweep rate might indicate that the quantity of charge consumed under the area of the first half cycle increased with the increase in scan rate. On integration the area gave the number of coulombs passed which is the amount of the species adsorbed at the electrode surface, reported in terms of miIli-couiombs in Table 1. According to Damaskin (1971) if an organic substance adsorbed on an electrode can be oxidised or reduced in a certain potential range, it is possible to estimate the adsorption of the substance from the quantity of electricity consumed for its oxidation or reduction. A plot of the adsorbed amount (miIli-couiombs) against the square root of scan rate showed inverse proportionality (Fig. 3). It could be indicated that the adsorption increases with the increase in scan rate. This is in agreement with the observation of Lagercrantz (1964) that the amount of adsorbed material is small at the sufficiently fast scan rate and at a moderately slow scan rate.

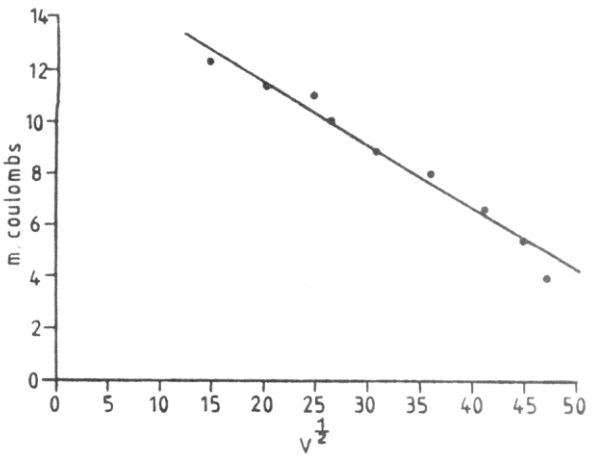


Figure 3. A plot of the adsorbed amount of riboflavin against the square root of scan rate.

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