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ANODIC VOLTAMMETRIC STUDY OF ASCORBIC ACID AT PLATINUM AND GOLD ROTATING DISC ELECTRODES

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ABSTRACT

Anodic Voltammetry of ascorbic acid at platinum and gold rotating disc electrodes has been examined in acidic and alkaline media. Ascorbic acid is oxidised by a single two electron wave at platinum and one electron two step at gold electrode. The best medium for electro-analysis is 0.1 mol 1^{-1} sulphuric acid in which it shows obedience to the Levich relationship at both electrodes. The limiting current is linearly proportional to ascorbic acid concentration with Zero intercept and shows excellent rapid voltammetric determination. Electrode Kinetic parameters for mass and charge transfer have been determined. Voltammetric method has been used to determine the number of electrons involved in the reaction and the reaction mechanism has been elucidated.

Introduction

Ascorbic acid (Vitamin C), is an important vitamin whose main functions are associated with scurvy, defective wound healing and increased fragility of blood vessels (Hughes, 1977). In addition to its therapeutic application ascorbic acid is also used as a processing aid in the brewing, backing and meat curing industries which increase the daily consumption of the vitamin. It is also used as an antioxidant in the pharmaceutical and food industries (Borenstein, 1965).

The megadose of ascorbic acid has an influence in the excretion of oxalic acid which is the end product of vitamin metabolism. the small increase of oxalic acid in the presence of calcium could enhance the formation of calcium oxalate which has low solubility in urine and hence increases the tendency of stone formation (Hughes, 1977). Megadosage of ascorbic acid also causes deep vein thrombosis (Horrobin, 1973) and hence its redox behaviour is an important factor in the metabolic disorders leading to the development of the disease.

Until recently no study of ascorbic acid oxidation at the rotating disc electrode has been conducted and no information is available on the electrode Kinetics of the reaction. Some polarographic studies of the redox reactions of ascorbic acid at drop-ping mercury electrode have been reported (Ratzkowski and Koral, 1977, Ruiz et al., 1977, 1978, Bourgeoes and Mainguy, 1975). Electrochemical studies at Tubular carbon electrode (Manson et al., 1972) showed one oxidation wave at pH less than 8 and two waves in alkaline media. At platinum microelectrode it revealed one two electron oxidation wave, at gold electrode two anodic waves were observed (Skobets and Atamanenko, 1949). Cyclic Voltammetry at platinum micro-electrode indicated reproducible oxidation for the vitamin in blood serum. The technique was also used for monitoring ascorbic acid in the kidney after intravenous injection and its function as an electrochemical indicator (Koryta at al., 1971). In the present investigation we wish to report the voltammetric study of the oxidation behaviour of ascorbic acid using platinum and gold rotating disc electrodes.

Experimental

Ascorbic acid of the pharmacopoeia) grade was kindly supplied by the Glaxo Laboratories U.K. The apparatus, instrumentation, electrode activation and its associated electronic, voltammetry, coulometry reagents and solution handling have been previously described (Bishop and Hussein 1984). Normal scan speeds were $5mVS^{-1}$ and the geometric area of the platinum and gold electrode were 0.503 cm^2.

Results and Discussion

Voltammetry of Ascorbic acid in acidic media

At platinum electrode ascorbic acid in 0.1 mol 1^1 sulphuric acid gave a single anodic wave with a well defined limiting current (Fig.1a) which is proportional to the square root of the rotation speed (Fig.2a) and concentration (Fig.2b) with zero intercept. There was little deactivation of the electrode as the offset repeat scan indicated the shifting of the wave to a more positive potential whilst the limiting current decreased. In 0.1 mol 1^1 perchloric add the wave shifted to a more positive potential on increasing the rotation speed thereby causing the shift of the half wave potential at a more positive (Fig.1b). A linear relationship was obtained between the half wave potential and square root of rotation speed (Fig.2c).

At gold electrode in 0.1 mol 1^1 sulphuric acid ascorbic acid showed two anodic waves (Fig.1c) which are more pronounced at higher rotation speeds and exhibit the peculiarity as observed by the overlapping of the waves. This overlapping could be assumed to be due to the adsorption of the anion radical (Gilman, 1966), Niedrach and Tochner, 1967, which is the active intermediate in the anodic oxidation of ascorbic acid

and showed the behaviour of two waves. In perchloric acid the similar characteristic was observed as on platinum electrode (Fig. ld, 2d).

Voltammetry of Ascorbic acid in alkaline Media

At platinum electrode ascorbic acid in 0.1 mol 1^{1} sodium carbonate gave two oxidation waves, one is poorly defined at - 0.1V Vs SCE whilst the other is well defined with dear limiting current (Fig.3a). The voltammograms are not in sequence with the rotation speeds and so can not be regarded as obeying the Levich equation (Levich, 1980). At gold electrode it exhibit three anodic waves, the first wave is ill defined at - 0.1V Vs SCE, second wave moderately defined at 01V Vs SCE while the third wave shows the enhance mass transfer with a peak at 0.5V Vs SCE, after the peak the voltammogram showed a through region (Fig.3b). This behaviour could be due to the adsorption of the oxidation product. The waves are not mass transfer con-trolled as is evident from the overlapping and intersecting of each other. The two anodic wave at platinum and three at gold in basic medium may be due to the decomposition of the reactant and rupture of the lactone ring (Ono et al., 1967).

Analytical Validity

Calibration results for the oxidation of ascorbic acid at platinum and gold electrode are given in Table 1 along with the precision of the data for determination of the vitamin at the alternative electrode. To appraise the reliability of rapid determination a series of four solution of ascorbic acid was prepared as a single measurement of the limiting current was made at each of the rotation speeds. The concentration was calculated from the slope and intercept and the percentage and relative standard deviation of each five determination are given in Table 2. This involves the propagation of error in rapid setting of the rotation speed. Each set of measurement requires less than 10 minutes including activation of the electrode. The relative standard deviation is well within 1%.

Determination of n Value

The number of electrons, taking part in the over all electrode reaction was determined by voltammetry of an ascorbic acid solution half oxidised by cerium IV in 0.1 mol 1^{-1} sulphuric acid. Firstly the voltammetric curve of freshly prepared ascorbic acid solution was recorded at a platinum electrode. Another scan with the fresh solution of ascorbic acid together with cerum lll (equivalent to Cerium IV) was recorded showing the identical limiting current to the the previous curve (without Cerium III). Finally, the voltammogram was recorded with ascorbic acid part oxidised by the addition of half an equivalent of Cerium IV. The resulting current was found to be *25%* less than that of the first and second scan (i.e. ascorbic acid and ascorbic acid plus cerium III). This gives a value of n=2 and is in agreement with previous data obtained via coulometric method (Rucda, et al., 1978, Mushran, 1977, Borensteen, 1965 and Ono et al., 1958). The

reaction mechanism for the electrooxidation of ascorbic acid involving two electrons is shown in Fig. 4.

Electrode Kinetics

The half wave potentials, mass and charge transfer rate constant and charge transfer coefficient β have been determined over a range of conditions and tabulations of values are available from the authors. The values have been calculated by pattern theory (Bishop, 1972) and are referenced to the half wave potential because condition-al potentials are not accessible. Half wave potentials are about 05V Vs SCE charge transfer rate constants range from 2.9 to 6.5 x 10^{-6} 1 cm 2 S.1 and charge transfer coefficients show very little variation around 0.28.

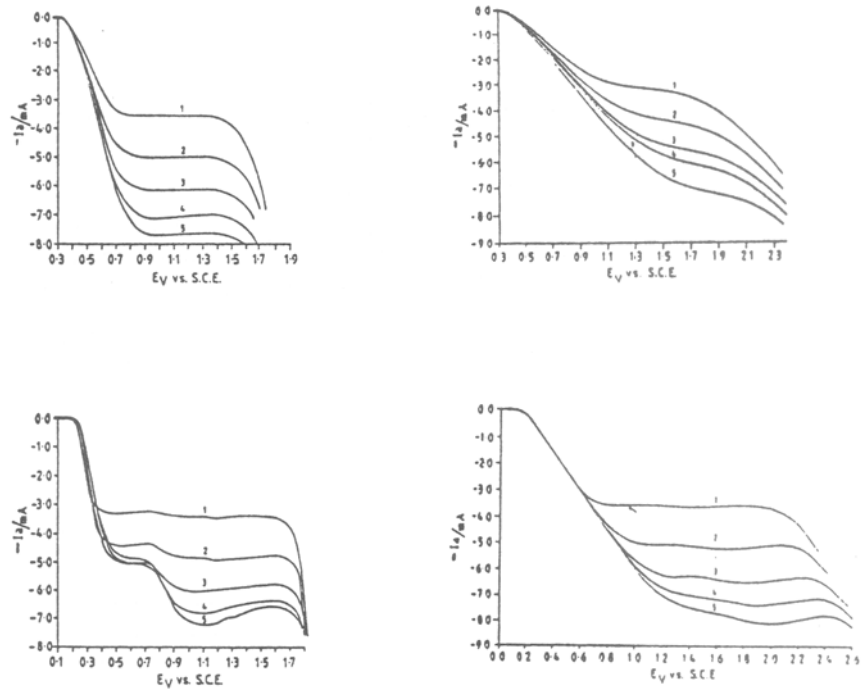

Fig. 1: Anodic Voltammograms of ascorbic acid, 5 x 10^4 mol 1^{-1} in 0.1 M sulphuric acid at (a) platinum and (C) Gold electrodes; in 0.1 M perchloric acid at (b) platinum and (d) gold electrode; electrode area 0.503 Cm^2, scan speed 5mVs ^{t} nominal rotation speed for curves 1-5 are 10, 20, 30, 40 and 50Hz respectively.

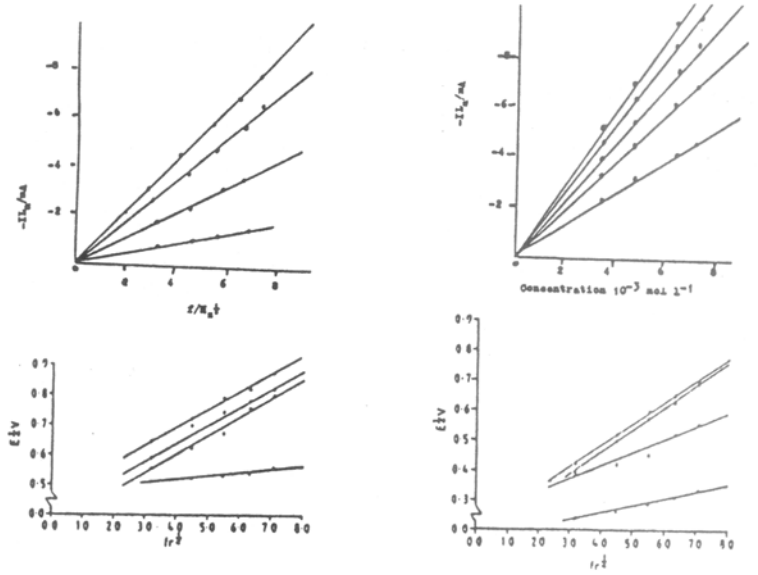

Fig. 2: Levich plots of limiting current (a) against square root of frequency, (b) against concentration of ascorbic acid 2, 5, 8 and 10 x 10^{-3} mol 1^4 at platinum electrode in 0.1 M sulphuric acid, nominal rotation speed in order of increasing current 10, 20, 30, 40 and 50 Hz. Variation of half wave potential on increasing the rotation speed in 02M perchloric acid at (c), platinum and (d) gold electrodes.

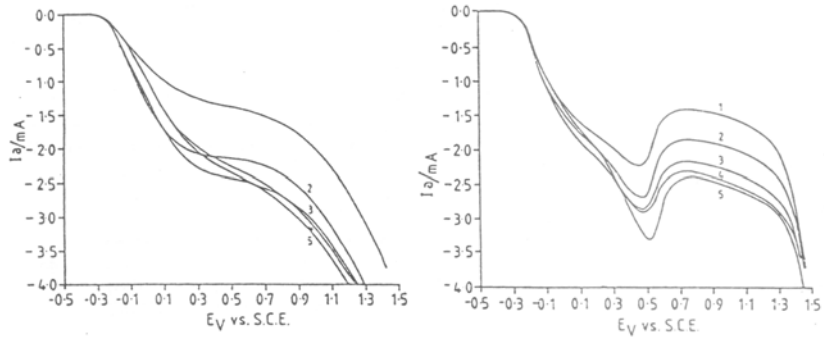

Fig. 3: Anodic Voltammograms of ascorbic acid, 5 x 30^{-3} mol^{l} in 0.1M sodium carbonate at (a) platinum (b) gold electrodes (area 0.503Cm^2), scan rate 5mVs^{-1}, temp. 25°C. The waves are not in accordance of rotation speeds, i.e. 10, 20, 30, 40 and 50Hz.

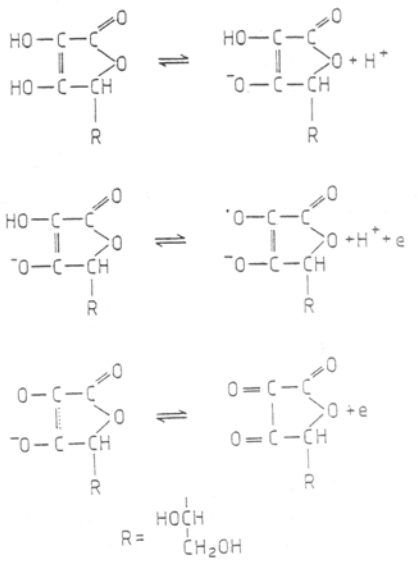

Fig. 4

Table 1

Calibration results for ascorbic acid at platinum and gold rotating disc electrodes area 0.503 Cm^2, medium 0.1M sulphuric acid,temperature 25°C and n = 2

Calibration analysis

Sample	Nominal Rotation Speed/HZ	Slope/ mA 1m mol l^{-1}	Intercept/ mA	Correlation Coefficient mA	SD of residuals/ 1m mol 1-1	SD of Slope/ mA	RES of Slope %
Ascorbic acid 0-5 x 10^{-3} mol l^{-1}							
Platinum electrode	10	0.39915	0.03412	0.99871	0.05139	0.01160	2.09
	20	0.47841	0.01652	0.99965	0.02296	0.00645	1.25
	30	0.51425	0.01962	0.99768	0.01989	0.00171	1.46
	40	0.57980	0.00345	0.99999	0.00251	0.00521	0.26
	50	0.60542	0.01154	0.99989	0.00653	0.00485	0.35
Gold electrode	10	0.46252	0.84561	0.99999	0.006894	0.00118	0.26
	20	0.66210	0.00576	0.99897	0.00094	0.00146	0.29
	30	0.62581	0.25621	0.99989	0.00586	0.00094	0.42
	40	0.58241	0.74121	0.99979	0.02249	0.00648	0.14
	50	0.69251	0.84092	0.99999	0.00016	0.01139	1.05

Table 2

Precision of determination by rotating disc electrode each result arises from the measurement of the limiting current at each of the five rotation speed. Electrode areas 0.503 Cm^2, medium 0.1M sulphuric acid and temperature 25°C.

Platinum Electrode		Gold Electrode	
Ascorbic acid 10^{-3} mol l^{-1}	RSD %	Ascorbic acid 10^{-3} mol l^{-1}	RSD %
1.9652	2.71	1.9913	1.07
4.9228	1.85	4.9974	0.07
7.9891	2.89	7.9987	2.45
9.9943	1.17	9.9965	1.33

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