E2-24: Mechanism of electron transfer between L-ascorbic acid and Pt disc electrode in neutral aqueous medium

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L-Ascorbic acid is easily oxidised to dehydro-l-ascorbic acid, and then hydrolysed to 2,3-dioxo-L-gulonic acid in neutral and alkaline media.The study of the oxidation mechanism of l-ascorbic acid is important due to many reasons. Such a study would be helpful in, understanding the metabolism of ascorbic and in living organisms, designing preventive measures for the aerial oxidation of l-ascorbic acid present in fruits and devising electrochemical sensors for the detection of ascorbic acid, etc. Thus a cyclic voltametric study of l-ascorbic acid, in aqueous solution, on a Pt disc electrode surface was carried out.

The chemicals used were of the highest available purity. Sodium perchlorate (Analar, Aldrich) and l-ascorbic acid (Surchem Products Ltd.) were used without further purification. Electrochemical studies of l-ascorbic acid were performed in a one compartment cell comprising a Pt-disc working electrode (WE), a saturated calomel reference electrode (SCE) and a Pt-gauze counter electrode. The reference electrode was placed very close to the WE in order to ensure the minimisation of the IR drop through the solution. All potentials quoted are with respect to SCE. Voltage scanning and potentiostating the WE were achieved with an electrochemical analyser (Oxford Electrodes) and the signals recorded on a chart recorder (Yew model). The solutions were deoxygenated by purging with O_2 free N_2 gas 30 min prior to the application of the potential and all electrochemical experiments were carried out under a N_2 gas blanket. In a typical experiment, the required quantity of l-ascorbic acid was dissolved in 0.100 mol dm^{-3} $NaClO_4$(aq) solution and deoxygenated. The cyclic-voltametric behaviour of the system of Pt-disc electrode was studied by changing the concentration on l-ascorbic acid from 1 mmol dm^{-3} to 10 mmol dm^{-3} in 1 mmol dm^{-3} increments. The scan rate dependence of the cyclic voltametric peaks was studied at scan rates of 10,20,50,100,200,500 and 1000 mV s^{-1}.

The cyclic voltametric behaviour of l-ascorbic acid in aqueous 0.100 mol dm^{-3} NaClO$_4$ solution on Pt-disc electrode is well defined with 2 oxidation peaks of the same size in the forward scan and 2 reduction peaks of different heights in the reverse scan. The oxidation peaks are centred at 340mV (peak 1) and 500mV (peak 2). The reduction peaks are centred at 300 mV (peak 1') and 600 mV(peak 2'). Repeating the CV in the range-0.80 V to 0.00 V gave only peaks 1 and 1' and in the range 0.00 V and + 1.00 V gave peaks 2 and 2' suggesting that 1 and 1' and, 2 and 2' are due to 2 different redox processes. This result also shows that a clean Pt surface is not essential for the adsorption of ascorbic acid unlike in the adsorption of other organic substances on Pt. Peak currents were found to be linearly proportional to the concentration of l-ascorbic acid for all 4 peaks and as such both redox processes involve l-ascorbic acid. The scan rate dependence of peak positions and currents of the peaks 1 and 1' has the following characteristic features:

i) $\Delta E_p = E_p^a - E_p^c \neq \frac{59}{n}$ mV, where n = 0, 1, 2, ...

ii) $|E_p - E_{p/2}| \neq \frac{59}{n}$ mV

iii) $\left|\frac{I_p^a}{I_p^c}\right| = 1$

(iv) I_p increases with $v^{1/2}$ but not proportional to it.

(v) E_p shifts towards cathodic direction for the reduction peak and towards anodic direction for the oxidation peak.

These features clearly show that the redox process responsible for peaks 1 and 1' occurs according to a quasi-reversible mechanism. Analysis of scan rate dependence of data for peaks 2 and 2' reveals that the closest mechanism is EC(i.e the electron transfer is followed by a chemical reaction.) The oxidation peak 2 is, therefore, due to the oxidation of L-ascorbic acid to dehydro-L-ascorbic acid its subsequent transformation to 2,3-dioxo-l-gulonic acid.

The electrochemistry of l-ascorbic acid in aqueous electrolyte on Pt-disc electrode is well defined with characteristic redox processes with different overvoltages. The 2 processes are well separated. One of the 2 processes may be due to electron transfer followed by a chemical reaction involving the formation of dehydro-l-ascorbic acid and its subsequent transformation to 2,3-dioxo-l- gulonic acid. The other process is quasi-reversible.