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Polarography of flavone and quercetin

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Electro-reduction behaviour of flavone (1,4-benzopyrone) and quercetin (3,5,7,3′,4′-pentahydroxy-1,4-benzopyrone) are reported over the entire pH-range using DC, AC and Kalousek polarographic methods, CV and controlled potential coulometry (stirred Hg pool cathode). Products of controlled potential electrolysis have been identified. Heterogeneous rate constants have been computed and reduction schemes proposed.

Flavones and flavonols belong to an important group of natural products which have high antioxidant properties and vitamin P activity. They are widely used for preservation of food products and as drugs for prevention of fragility of blood vessels. Since their redox behaviour is mainly responsible for the above properties, their organic polarography had been carried out by earlier workers. Further, this method has been used to identify and estimate the above compounds.

Geissman *et al.*[1] examined DC polarograms of some flavones, flavanones and flavonols under limited set of conditions. Later studies[2] were also not exhaustive.

The studies covered neither a wide pH-range nor extensive electrometric investigation. Therefore, the present investigation was undertaken to study the polarographic behaviour of flavone and quercetin (a flavonol) over the entire pH-range using DC, AC and Kalousek polarographic methods, CV and controlled potential coulometry. UV-VIS spectroscopy was conducted to identify the products of controlled potential electrolysis.

Results and Discussion

Flavone :

DC polarograms of flavone were single waves at pHs 2.1 and 3.2, two waves at pH 3.2–7.4, unsymmetrical single waves at pHs 9.4 and 10.6 and unsymmetrical wave followed by another small more negative wave at each of pHs 11.6, 12.2 and 13.1. The total limiting current was nearly constant at pH $\geq$ 4.3, whereas it had about half this value at pHs 2.1 and 3.2, presumably because of merger of the second wave with that of the supporting electrolyte. The $E_{1/2}$ vs pH slopes for the first wave were –0.089 and –0.015 V per pH-unit, the linear plots meeting at pH 8.0. Plots for the second wave had slopes –0.0 and –0.022 V per pH-unit, which met at pH 10.6. The plot for the third wave was independent of pH.

The limiting currents of flavone were linear functions of concentration (0.2–1.09 mmol dm^{-3}) and of $h^{2/3}$ (controlled drop-time 2 s; pH 6.2) for both the waves, indicating their diffusion-controlled nature.

That two faradays were involved in the reduction process was established by comparing the I-value (2.412 μA mmol^{-1} dm^3 mg$^{-2/3}$ s$^{1/2}$ at pH 6.2) with that for xanthone (I = 2.443 μA mmol^{-1} dm^3 mg$^{-2/3}$ s$^{1/2}$ at pH 6.2), which for the latter compound was established by millicoulometry and CPC (at stirred Hg pool cathode)[3]. Kalousek polarogram (pH 6.2) did not exhibit any anodic wave[4], indicating irreversibility of the reduction process. Heterogenous rate constants ($k^0_{f,h}$) at pHs 3.2 and 12.0 were 1.259×10^{-10} and 1.0×10^{-16} cm s^{-1} respectively[5].

Cyclic voltammograms (HMDE) at pH's 3.3, 6.2, 8.1, 11.6 and 13.0 revealed no anodic peak indicating irreversibility of the cathodic process (Fig. 1). Cathodic peak potentials shifted to negative values with increasing scan-rate, also establishing irreversibility. Cathodic peak currents were linearly proportional to concentration and to $v^{1/2}$

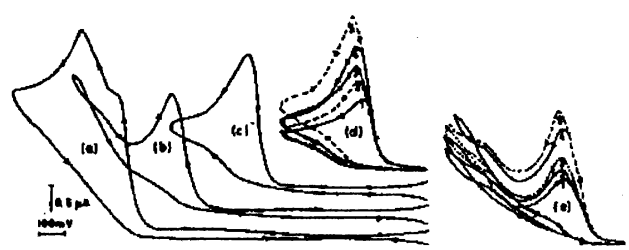

Fig. 1. Cyclic voltammograms of flavone (0.4 mmol dm^{-3}) : (a) pH 13.0, scan range (right to left) = –0.3 to –1.8 V, scan rate = 0.15 V s^{-1}, (b) pH = 6.2, scan range (right to left) = –0.3 to –1.6 V, scan rate = 0.15 V s^{-1}, (c) pH = 3.2, scan range (right to left) = –0.3 to –1.2 V, scan rate = 0.15 V s^{-1}, (d) pH = 3.2, scan range (right to left) = –0.7 to –1.2 V, scan rates = 1 to 5 : 0.05, 0.075, 0.10, 0.15 and 0.20 V s^{-1}, and (e) pH = 6.2, scan range (right to left) = –0.9 to –1.6 V, scan rates = 1 to 5 : 0.064, 0.075, 0.10, 0.15 and 0.20 V s^{-1}.

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(v = scan-rate) and the plots passed through the origin, signifying diffusion-controlled nature of the electrode process; $ip/v^{1/2}$ was independent of v, indicating uncomplicated charge-transfer process[6]. The αn_a value calculated from $E_p - E_{p/2} = -0.048/\alpha n_a$ relationship was unity over the whole pH-range.

AC polarograms (Fig. 2) corresponded nearly to DC polarograms and their peak currents were linear functions of concentration. Further, their baselines were above those of the supporting electrolyte, indicating absence of any adsorption process. Constant potential electrolysis (20 cm^3, 1.0 mmol dm^{-3}, pH 7.5; –1.55 V) was carried out till reduction was apparently complete (2 h). The UV-VIS spectra[7] before and after electrolysis and also that of the product of

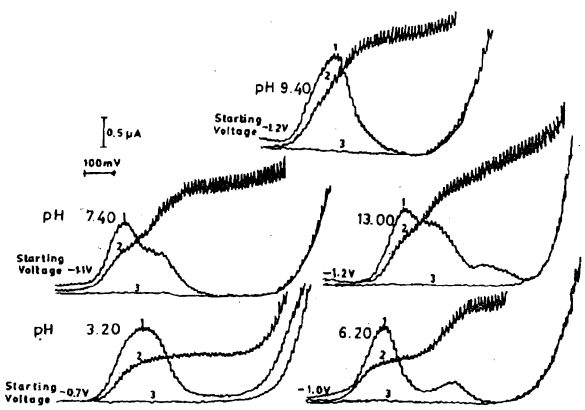


Fig. 2. AC and DC polarograms of flavone (0.4 mmol dm^{-3}) : (1) AC polarograms, (2) DC polarograms and (3) AC polarograms of base electrolyte.

electrolysis in 1.0 *N* HCl (Fig. 3) proved that the reduction product was 4-hydroxyflavene (II), which yielded flavylium chloride (V) in 1.0 *N* HCl (band at 398 nm). Constant potential coulometry (0.02012 mmol, pH 8.4; –1.5 V) at stirred Hg pool cathode, however, exhibited consumption of four faradays per mole, which proved that 4-

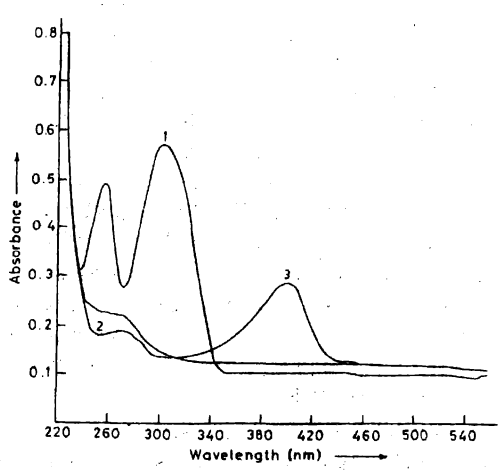
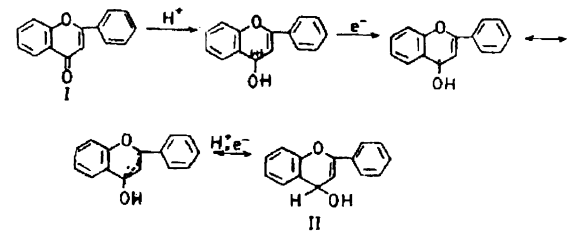


Fig. 3. Electronic spectra of flavone : (1) flavone (0.02 mmol dm^{-3}), pH = 7.2, (2) reduction product of flavone, pH = 7.2 and (3) reduction product (pH = 7.2) of flavone in 1.0 *N* HCl.

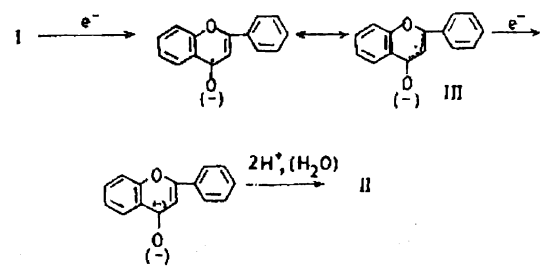
hydroxyflavene (II) formed by a two-electron process, was further reduced to 4-hydroxyflavan (VI) under these conditions.

Mechanism of reduction of flavone : (i) In acidic solutions, high $E_{1/2}$ vs pH slope indicated protonation before electron-transfer and a CEEC mechanism has been suggested (Scheme 1). (ii) In the higher pH-range (≥8.4) both



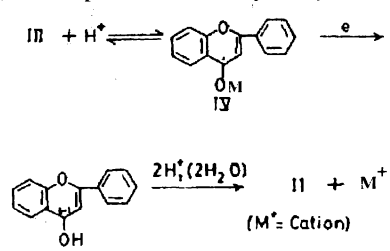
Scheme 1

the $E_{1/2}$ values were more or less pH-independent and an EECC mechanism (Scheme 2) is proposed. (iii) At still



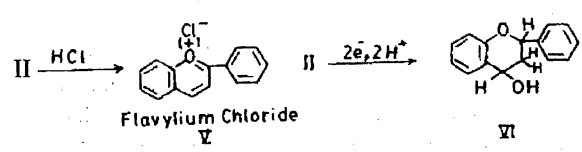
Scheme 2

higher pH's (≥11.6) where another more negative DC wave was seen, metallation of one-electron reduction product (radical-anion, III) has been proposed. The resulting radical (IV) underwent reduction at more negative potentials (Scheme 3). The product II (4-hydroxyflavene) yielded



Scheme 3

flavylium chloride (V) on acidifying its solution (band at 398 mm), which in CPC (pH 8.4) yielded 4-hydroxyflavan (VI) due to its continuous electrolysis (Scheme 4).



Scheme 4

Quercetin :

It exhibited a single DC wave in the pH-range 5.2–11.5, with nearly constant limiting current. The $E_{1/2}$ vs pH slopes

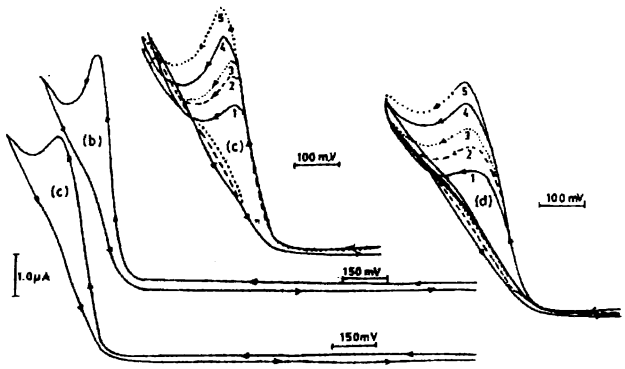


Fig. 4. Cyclic voltammograms of quercetin (0.4 mmol dm^{-3}) : (a) pH = 8.2, scan range (right to left) = –0.3 to –1.8 V, scan rate = 0.15 V s^{-1}, (b) pH = 6.2, scan range (right to left) = –0.3 to –1.8 V, scan rate = 0.15 V s^{-1}, (c) pH = 6.2, scan range (right to left) = –1.2 to –1.7 V, scan rates = 1 to 5 : 0.05, 0.075, 0.10, 0.15 and 0.20 V s^{-1} and (d) pH = 8.2, scan range (right to left) = –1.3 to –1.8 V, scan rates = 1 to 5 : 0.05, 0.075, 0.10, 0.15 and 0.20 V s^{-1}.

of the two linear portions of the plot were –0.039 and –0.091 V per pH unit, the two lines meeting at pH 8.2. The limiting current was linearly proportional to concentration (0.4–1.053 mmol dm^{-1}, pH 7.2) and to $h^{2/3}$ (controlled drop-time 2 s, pH 7.2) indicating diffusion-control. The *I*-value, 2.536 μA $mmol^{-1}$ dm^3 $mg^{-2/3}$ $s^{1/2}$ at pH 6.2 matched with that for xanthone, 2.443 μA $mmol^{-1}$ dm^3 $mg^{-2/3}$ $s^{1/2}$ at pH 6.2, indicating a two-electron reduction process. The

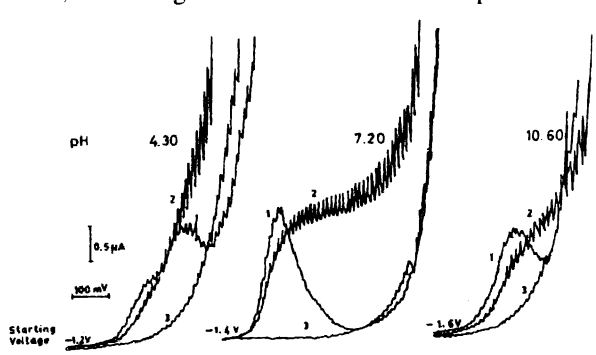


Fig. 5. AC and DC polarograms of quercetin (0.4 mmol dm^{-3}) : (1) AC polarograms, (2) DC polarograms and (3) AC polarograms of base electrolyte.

$k^0_{f,h}$ values were 1.0×10^{-27} cm s^{-1} at pH 5.2 and 6.31×10^{-26} cm s^{-1} at pH 9.7, showing an irreversible reduction of quercetin.

The CV voltammograms (HMDE) revealed one cathodic and no anodic peak at different pH-values (Fig. 4), the peak potentials shifting towards negative values on increasing scan-rate (v), which also proved irreversible nature of the reduction process. However, the i_p vs $v^{1/2}$ and i_p vs C plots were linear and passed through the origin, confirming diffusion-control. The $i_p/v^{1/2}$ vs v plots were horizontal straight lines, which showed uncomplicated charge-transfer process. The αn_a value obtained from E_p and $E_{p/2}$ values was nearly unity.

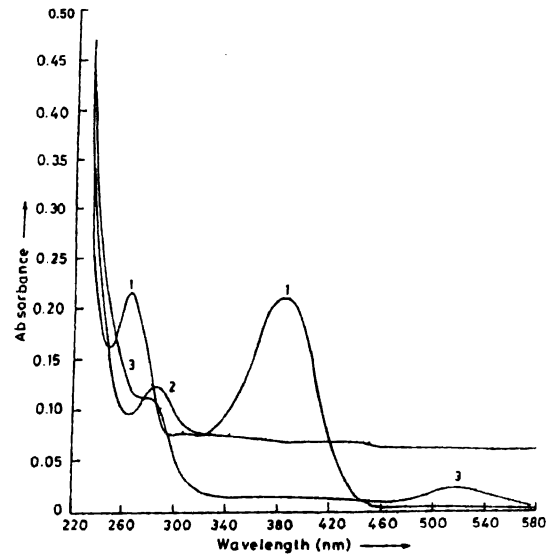


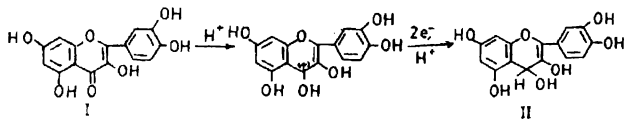
Fig. 6. Electronic spectra of quercetin : (1) quercetin (0.01 mmol dm^{-3}), pH = 7.2, (2) reduction product of quercetin, pH = 7.2 and (3) reduction product (pH = 7.2) of quercetin in 1.0 *N* HCl.

AC polarograms (Fig. 5) corresponded the DC polarograms, excepting that at pH 4.3 a shoulder is seen at more positive potentials in addition to the AC peak; this may be due to reduction in two steps at this pH-value. At high pH-values (12.0 and 12.7) no AC peak could be seen, probably due to pre-discharge of the base electrolyte. As in the case of flavone, the base lines of these AC polarograms were above those for the supporting electrolyte (in the absence of quercetin), proving absence of adsorption of quercetin and its reduction products at the DME.

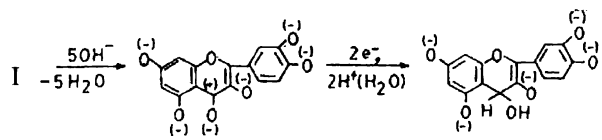
Controlled potential electrolysis (20 cm^3, 1.0 mmol dm^{-3}, pH 7.2, –1.65 V) carried out for two hours appeared to complete the reduction (wave-height zero). The UV-VIS spectra (Fig. 6) taken before and after electrolysis and also that for the final solution in 1.0 *N* HCl (colour turned red on addition of HCl) showed an additional band at 530 nm for the last solution, which matched that for cyanidin chloride[7]. This result proved that under these conditions, a 4-hydroxyflavene derivative (II) was produced by a two-faraday process, similar to that given by flavone on CPE.

Coulometry at stirred Hg – pool cathode (0.0203 mmol, pH 8.9, –1.6 V) exhibited a four-faraday process, indicating further reduction of the two-electron reduction product (II) under these conditions, yielding, presumably, a 4-hydroxyflavan derivative (III).

Mechanism of reduction of quercetin : (i) In acidic solutions, $E_{1/2}$ vs pH dependence of waves indicated, at least, one proton-transfer prior to the electrode process (CEEC; Scheme 5). (ii) For alkaline solutions (pH ≥ 8.2) the high pH-dependence may be due to reduction of polyanionic forms of quercetin (Scheme 6). (iii) That the two-electron

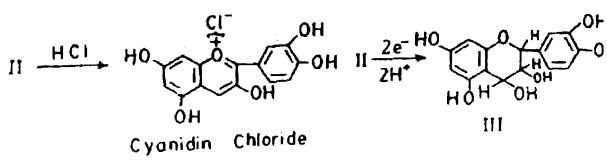


Scheme 5



Scheme 6

reduction product is 4-carbinol, >CHOH, is proved by the formation of cyanidin chloride (red in colour, band at 530 nm) on addition of HCl to the CPE product. The four-electron reduction product in CPC, is the 4-hydroxyflavan derivative (III) (Scheme 7).



Scheme 7

Experimental

Bruker Universal E 310 modular polarograph with Hewlett-Packard 7050A X-Y recorder was used for the polarographic and CV studies. For CPC, a digital coulometer (model 640, Electrosynthesis Co., U.S.A.) was used to apply the required potential, and the extent of electrolysis was monitored by recording polarograms with a dme fitted into the electrolytic H-type cell. UV-VIS spectra was recorded using a Cecil CE 599 spectrophotometer. The pH-values were checked with an Elico LI 120 pH meter.

Capillary used had characteristics, m = 1.293 mg s^{-1} and t = 4.1 s at 40 cm height of Hg reservoir, and controlled drop-time of 2 s was used for recording the polarograms.

The test solutions contained ethanolic depolarizer solution (4.0 mmol dm^{-3}; 2.5 cm^3), aqueous acetate-phosphate-borate universal tetramethylammonium buffer (12.5 cm^3; 0.026 mol dm^{-3} of each salt), additional ethanol (10 cm^3) and calculated amounts of tetramethylammonium bromide, and made upto 25 cm^3 with distilled water, making the final solution 0.4 mmol dm^{-3} in depolarizer, 0.04 mol dm^{-3} in buffer, 0.1 mol dm^{-3} in ionic strength and 50% (v/v) in ethanol. The pHs given in the figures are the apparent pH-values of these solutions. For CPC and CPE, the concentrations of the depolarizer have been given at appropriate places.

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