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Short communication

The novel water soluble flavonoid dihydroquercetin monosuccinate: A cyclic voltammetry

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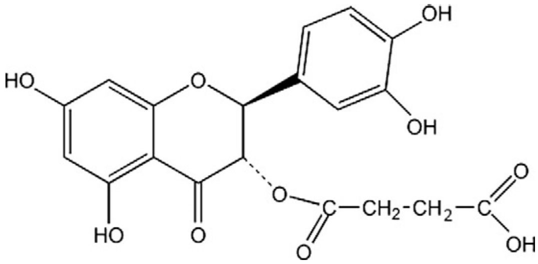
ABSTRACT

A novel water soluble antioxidant, dihydroquercetin monosuccinate electrochemical transformations have been studied on the graphite electrode in a wide range of pH. In contrast to acidic solutions, in basic media dihydroquercetin monosuccinate redox transformations have a weak diffusion control, and occur in the close to electrode surface layer. The number of protons transferred per one electron for different conditions has been elucidated.

1. Introduction

Recently dihydroquercetin monosuccinate *4[2-(3,4-dihydroxyphenyl)-5,7-dihydroxy-4-oxo-3,4-dihydro-2H-chromen-3-yl]-3-carboxypropanoate* (DHQMS), a synthetic derivative of the native antioxidant dihydroquercetin (DHQ) has been synthesized in order to get a novel substance with antioxidative properties that is at the same time more water soluble than parent compound [1].



A weak solubility of DHQ in water and in fats impedes its utilization as a component of preparations for injection, drops, etc. Modification of the DHQ molecule by hydrophilic substitutes keeping intact the fragments responsible for antioxidant properties is a promising way to obtain water soluble derivatives. The succinic acid residue linked to DHQ is the possible substitute for this strategy.

In vivo biotransformations of such a molecule would produce succinic acid — nontoxic and easily metabolizable compound. DHQMS solubility is 1.73 g per 100 g water. This value is 42 times higher comparing to parent DHQ.

Dihydroquercetin electrochemical behavior has been studied extensively [2–4], although the mechanism of DHQ redox transformations and its peculiarities are still a subject for discussion. To our knowledge there is no data for electrochemical properties of the novel DHQ derivative except our previous paper [1] where the DHQMS antioxidant activity and a complex character of the redox transformations on the graphite electrode have been demonstrated. The TEAC [5] values measured for DHQMS and DHQ are close to each other confirming that oxidative transformations of these substances are similar at least in the in vitro experimental conditions. In the present study we made an attempt to clarify the peculiarities of the novel water soluble antioxidant dihydroquercetin monosuccinate electrochemical transformations on the graphite electrode in a wide range of pH.

2. Materials and methods

Dihydroquercetin monosuccinate (>95%) was cordially provided by "Flavir" company (Irkutsk, Russia). Main characteristics of DHQMS were given in [1]. Potentiostate IPC — proM (Russia) and a three electrode cell (50 ml) have been utilized for electrochemical experiments. A graphite rod with visible area 0.39 cm^2 served as a working electrode. Silver chloride electrode BAS RE-1 and Pt plate were reference and auxiliary electrodes, respectively. Potential sweep rates (v) were varied in the range 1–500 mV/s. 0.1 M phosphate buffer solutions were the background electrolyte for all experiments. Before voltammetry measurements, argon was bubbled through the solution in the cell for 10 min. All experiments have been done at an ambient temperature.

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3. Results

According to Fig. 1 current values in the peaks of DHQMS oxidation and reduction (I_p) expectedly depend on the sweep rate. It's well known [6] that the character of this dependence could be determined either by diffusion controlled process or, alternatively, by redox transformations in the thin layer close to electrode surface. The linearization in $I_p - \sqrt{\nu}$ coordinates confirms the diffusion controlled mechanism whereas the linearization of $I_p - \nu$ dependence should be considered as an argument in favor of kinetic conditions of redox transformations. In our case the diffusion–kinetic control significantly depends on pH of the DHQMS solutions.

Fig. 2 presents both $I_p - \sqrt{\nu}$ and $I_p - \nu$ dependences for DHQMS oxidation and reduction at different pH values. The dependences clearly show that at pH 3.0 plot I_p vs $\sqrt{\nu}$ gives better linearization comparing to I_p vs ν implying a diffusion controlled redox process. However, this situation changes with pH increase. At pH 9.0 I_p both DHQMS oxidation and reduction peaks linearly depends on sweep rate value (Fig. 2 a). A good illustration of this nontrivial fact gives a logarithmic plot lg I (mkA) vs lg ν(mV/s) for DHQMS oxidation and reduction peaks (Fig. 3).

At pH 3.0 plots are linear with the slopes close to 0.5, confirming diffusion control. At pH 9.0 dependence of lg I vs lg ν for oxidation peak has an inflection point at $\nu = 20$ mV/s. The slopes for oxidation peak measured at $\nu > 20$ mV/s as well as for reduction peak measured into all ranges of sweep rates studied are close to 1, allowing for supposing of kinetic control and redox transformations occurring in the near to electrode layer. The slope of lg I vs lg ν for oxidation peak obtained at slow sweep rates ($\nu < 20$ mV/s) is less than 0.5 that again makes presumable the diffusion control.

Analysis of the data shown on Figs. 2 and 3 leads to the assumption that in contrast to acidic solutions in basic media DHQMS redox transformations on the graphite electrode have a weak diffusion control and occur in the close to electrode surface layer. Taking into account the difference in the total current values of DHQMS oxidation and reduction peaks in the pH 3.0 and 9.0 solutions it is obvious that observable peculiarities should be attributed to the DHQMS adsorption on the electrode surface. It is known that strong adsorption is characteristic for hydroquinone derivatives [7]. In order to confirm this assumption, immediately after measurements in DHQMS solution the electrode was extracted, thoroughly rinsed with twice distilled water and immersed in the fresh background buffer solution where a few cycles of voltammogram were taken. These results are shown in Fig. 4. The similarity of the cyclic voltammograms measured in background (curves 1) and DHQMS solutions (curves 2) both at pH 3.0 (Fig. 4a) and at pH 9.0 (Fig. 4b) and close potential values for oxidation and reduction peaks confirm a DHQMS presence on the electrode surface even after it was rinsed with water. In acid media electrode transfer from DHQMS solution into background one leads to significant decrease of the peak current values. In contrast, for pH 9.0 both for background and DHQMS solutions voltammograms are similar and give peak current values much less than in pH 3.0 solutions. It should be noted that a double layer capacity current remains apparently the same for all curves presented in Fig. 4. These observations do not contradict with the assumption that DHQMS adsorbs onto the electrode surface at all pH values studied although the adsorption influence should be different. At pH 9.0 the DHQMS oxidation and reduction processes take place preferentially on the electrode surface whereas at pH 3.0 a more probable mixed character with significant contribution of diffusion.

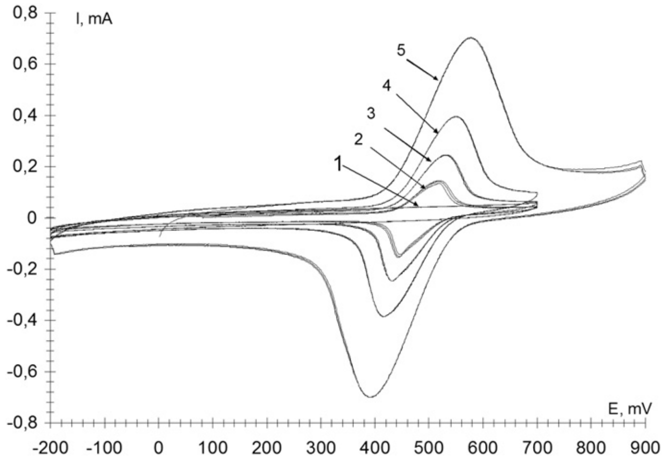

Fig. 1. Cyclic voltammograms measured on the graphite electrode in the background solution at $\nu = 20$ mV/s (curve 1) and in the DHQMS solutions ($C = 10^{-3}$ M) at $\nu = 5, 10, 20, 50$ mV/s (curves 2, 3, 4, 5, respectively); pH 3.0.

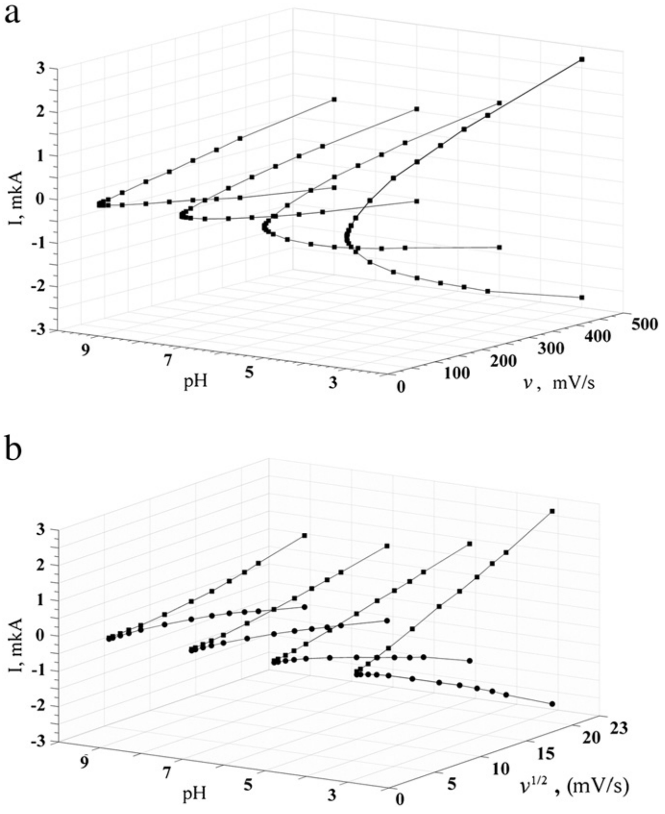

Fig. 2. Plots of DHQMS oxidation and reduction peak currents I_p vs ν (a) and $\nu^{1/2}$ (b) at different pH values.

DHQMS oxidation and reduction peak potential values strongly depend on solution pH (Fig. 5).

4. Discussion

Analysis of the data presented in Fig. 5 shows that for both anodic and cathodic peaks the dependences are linear in pH range studied but have an inflection point at pH about 5.0. Hence, one could assume protons' involvement into DHQMS electrochemistry. However the number of protons transferred per one electron differs for cathodic and anodic redox reactions and changes within pH window studied.

For an electrochemically irreversible system of interest the protons and electrons are transferred in separate steps. In this case, a main interest in voltammogram analysis consists in the potential values E_p for both reduction and oxidation [6]:

$$E_p = const + \frac{RT}{(n' + \alpha)F} \ln \frac{[H^+]^m}{K + [H^+]^m} \tag{1}$$