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The effect of solvents on the electrochemical behavior of homogentisic acid

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ABSTRACT

The electrochemical oxidation of homogentisic acid (HGA) as an important biological molecule has been studied in aqueous and mixed acetonitrile–water solutions using cyclic voltammetry. The effects of pH, HGA concentration, time window of the chosen electrochemical method and different solvents were studied to investigate the proton and electron transfer processes. The oxidation product of HGA in aqueous solution is stable in acidic, neutral and weakly alkaline media at the time scale of cyclic voltammetry. The electrooxidation process of HGA in aqueous solution follows E_q mechanism. In mixed acetonitrile–water solution, the electrooxidation process of HGA follows an $E_qC_iE_q$ mechanism. The experimental results indicate that the subsequent chemical reaction of dimerization is more probable for the oxidized form of HGA. It is shown that the separation of the cathodic and anodic peak potentials, ΔE_p, in the mixture of acetonitrile–water is greater than that in aqueous solution and it increases with the increase of acetonitrile content in the mixture.

1. Introduction

Hydroquinone derivatives (H_2Q) are widely used as reducing agents, antioxidants, polymerization inhibitors, black white film developers, anthraquinone dyes, azo dyestuffs and other chemical intermediates [1,2]. Besides chemical aspects, quinone couples play important roles in the biochemistry of living cells. The biological activity of these compounds has been related to their capacity to accept one or two-electrons generating reduced species, semiquinone radical anion ($Q^{\cdot -}$) and the dianion of hydroquinone (Q^{2-}) [3–5]. Thus, the study of mechanisms of biological action requires the understanding of the factors that modify redox properties and reduction mechanisms of quinone systems. Polarity of the solvents, nature of the supporting electrolyte, intra or intermolecular hydrogen bonding, presence of acidic or basic additives, ion pairing and protonation–deprotonation equilibrium play a crucial role in stabilizing reduced forms of quinones [6–8]. It is well documented that in hydroxyquinones, the position of hydroxyl functional group can alter the typical redox behavior of the quinonoid moiety in aqueous solution [9–11] owing to the hydrogen bonding interactions in the reduced species. Moreover, the electrochemical behavior of hydroquinones in aprotic solvents is different than that of benzoquinones, due to the intrinsic acidic properties of its oxidized form [12]. It is known that certain kinds of hydroquinones have noxious effects in biological systems by their intrinsic electrochemical properties and by the activity of the intermediate species that are formed during the oxidation process [13,14]. These characteristics make the electrochemical behavior of hydroquinones far more challenging to interpret than the corresponding quinones.

Homogentisic acid (HGA, see Scheme 1 for the structure) is a 2-substituted hydroquinone. It is an important intermediate in the metabolism of tyrosine and phenylalanine [15,16]. HGA in the body is readily oxidized to 4-maleylacetoacetic acid by HGA oxidase [17,18]. Therefore the amount of HGA in the body is extremely small. However, in a few individuals suffering from alkaptonuria [19], the HGA levels are found to be dramatically elevated in blood and urine. More studies have focused on the effect of HGA concentration in an alkaptonuria disease [20,21]. HGA is particularly interesting as there has been no report for any coupled chemical reaction for its redox form. Its oxidation mechanism is believed to be purely electrochemical (E) in nature, whereas the coupled chemical reaction can be observed for most monosubstituted *o*-benzoquinones [22–25]. Despite the biological importance of this compound, there are only few studies on the oxidation mechanism of HGA in protic and aprotic solvents [26–28]. Recently, we studied the oxidation reaction of HGA in aqueous solution and in mixture of acetonitrile and water [29]. We obtained thermodynamic variables of HGA oxidation, experimentally and theoretically

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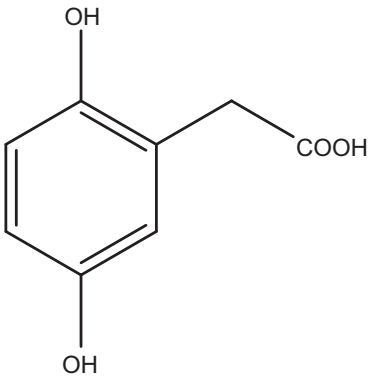

Scheme 1. The structure of homogentisic acid, HGA.

[29]. In this work, we study the electrochemical behavior of HGA in aqueous and mixed aqueous-acetonitrile solutions which have not been reported yet. The effects of different parameters such as solution pH, HGA concentration and time window of the chosen electrochemical method have been investigated in this work.

2. Experimental

Electrochemical measurements were performed with an Autolab/PGSTAT 101(Eco-Chimie) with the powerful NOVA software. A three-electrode electrochemical cell was employed for all the electrochemical measurements. The working, counter, and reference electrodes were a glassy carbon electrode with a diameter of 2 mm, a graphite electrode, and a saturated calomel electrode (SCE) respectively. All the potentials in the text were reported with respect to this reference electrode. The pH measurements were done with a Metrohm model 691 pH/mV meter. HGA was purchased from Acros Company. Acetonitrile, tetrabutylammonium perchlorate and all the other chemical reagents used for the preparation of buffer solutions were reagent grades from Merck Company and were used as received. The solutions were prepared with doubly distilled water. The buffer solutions were made from 0.1 M H_3PO_4 + NaH_2PO_4, and the pHs were adjusted with 0.1 M H_3PO_4 or 2.0 M NaOH. The surface of the glassy carbon electrode was hand-polished with 0.05 μm alumina–water slurry using a polishing cloth and was rinsed with doubly distilled water in order to avoid contamination of oxidation products and to obtain a clean renewed electrode surface. All solutions were freshly prepared and their voltammograms were recorded immediately. In all experiments, high-purity nitrogen gas (99.999%) was used for solution de-aeration before each experiment.

3. Results and discussion

3.1. Electrochemical behavior of HGA in aqueous solution

Fig. 1A shows the cyclic voltammograms at a glassy carbon electrode in a 0.1 M phosphate buffer solution (pH 3.0) containing different concentrations of HGA at 50 mV s^{-1}. The anodic peak is due to the oxidation of HGA to its corresponding *o*-benzoquinone derivative $(HGA)_{ox}$, and the cathodic peak is due to the reduction of the produced $(HGA)_{ox}$ to HGA. In order to investigate the stability of $(HGA)_{ox}$ on the time-scale of the used electrochemical method, the effects of an increase in the HGA concentration on the voltammetric responses in neutral and basic pHs were also studied, and the results are presented in the Supporting Information, SI, (Figs. S1 and S2 of the SI). When the product of oxidation process is stable at the electrode surface and does not participate in any following chemical reaction, the current of cathodic peak is equal to anodic peak and the ratio of I_{pc}/I_{pa} will be unity (inset of Fig. 1A).

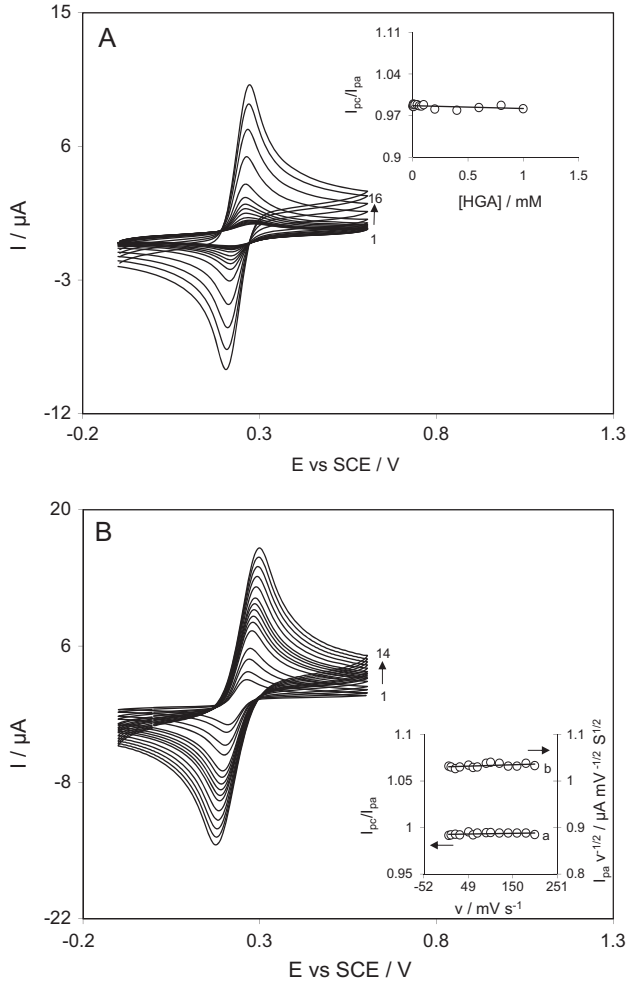

Fig. 1. (A) Cyclic voltammograms at a glassy carbon electrode (at 50 mV s^{-1}) in a 0.1 M phosphate buffer solution containing different concentrations of HGA in pH 3.0. Numbers 1–16 correspond to HGA concentrations of 1.0×10^{-3}–1.0 mM respectively. Inset: variations of the peak current ratio, I_{pc}/I_{pa}, vs. HGA concentrations. (B) Cyclic voltammograms at a glassy carbon electrode in a 0.1 M phosphate buffer solution containing 0.8 mM HGA in pH 3.0 at different potential scan rates. Numbers 1–14 correspond to potential scan rates 5–200 mV s^{-1}. Inset: variations of the peak current ratio, I_{pc}/I_{pa}, (curves a) and the scan rate normalized current, $I_{pa}/v^{1/2}$, (curves b) vs. potential scan rate.

Fig. 1B shows the cyclic voltammograms at a glassy carbon electrode in a 0.1 M phosphate buffer solution (pH 3.0) containing 0.8 mM of HGA at different potential scan rates. For more information about the electrochemical behavior of HGA, the effect of the potential scan rate in neutral and basic medium was also studied (Figs. S3 and S4 of the SI). The ratio of I_{pc}/I_{pa} versus potential scan rate at acidic, neutral and basic pHs are shown in inset of Fig. 1B, curve a, and inset B of Figs. S3 and S4 of the SI, curve a. As revealed by these figures, at all the studied pHs, even at slow scan rates in which the time characteristic (time window, τ) of the chosen electrochemical method is large, there is no possibility for any following chemical reaction and, therefore, the ratio of I_{pc}/I_{pa} is equal to one [30]. The results of current function ($I_{pa}/V^{1/2}$) versus potential scan rate in acidic (Fig. 1B, inset), neutral (Fig. S3 of the SI, inset B, curve b) and basic pHs (Fig. S4 of the SI, inset B, curve b) confirm that the oxidation product of HGA is stable in the time window of the voltammetric method. The results of potential scan rate study also confirm that $(HGA)_{ox}$, produced at the electrode surface, is