Electrode Processes of 1,2,4-benzenetriol in Different non-aqueous Solvents

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Abstract The electrooxidation of 1,2,4-benzenetriol was studied in different non-aqueous solvents. The results showed that the studied substance can be oxidized in several ways on the electrode surface due to the favourable positions of hydroxyl groups (similarly to hydroquinone, resorcinol and catechol). In most cases one anodic peak appeared involving all possible electrode processes. The concentration dependence of voltammetric peak currents using platinum macroelectrode showed nonlinearity attributable to the 1,3-oxidation similarly to resorcinol leading to partial deactivation. Appearance of more peaks indicated the weak deactivation at higher concentrations in acetonitrile and nitrobenzene. At higher concentration the microelectrode became deactivated as in the successive scans the currents declined continuously reinforcing the existence of resorcinol pathway.

Keywords: 1,2,4-benzenetriol, Microelectrode, Mesityl oxide, Non-aqueous solvents

1. Introduction

Quinones are compounds being able to undergo reversible oxidation/reduction electrode reactions and they are useful as antioxidant. The reversible charge transfer process is mainly characteristic of quinones having hydroxy groups in the 1,2 and 1,4 positions. Much less attention has so far been paid to electrochemistry of 1,2,4-benzenetriol (with other commonly known names hydroxyhydroquinone or hydroxyquinol) than to hydroquinone, catechol, resorcinol and pyrogallol which are very similar phenolic compounds to the compound studied here. The reports which target the exploring of hydroxyhydroquinone or related compounds are interested in it as intermediate of certain metabolisms and industrial processes predominantly in aqueous media [1-8].

The most of quinones have been widely investigated both in aqueous and non-aqueous environments [9-15]. Most of them show reproducible current signals. As 1,2,4-benzenetriol was studied only in aqueous solvents and mainly in concern of decomposition product of larger molecules and not related to electrochemistry in most works (for electrochemistry related publication see [16]) this work deals with its electrochemical properties in different non-aqueous solvents by using cyclic voltammetry for characterization.

In an earlier work resorcinol was one of the polyhydroxy phenols that showed fast electrode deactivation in the majority of non-aqueous solvents during its electrooxidation [17]. It is worth mentioning that numerous articles involving resorcinol electrooxidation are connected to determination of this compound in aqueous solvents in low concentrations. These concentrations were not enough for observing electrode fouling, so analytical procedures are based on obtaining reproducible current signals in the low concentration range. There is a detailed work for resorcinol polymerization which involves also the oxidative polymerization taking place at anodes in electrochemical experiments [18]. It reveals the variations of oxidation routes.

We found also that mesityl oxide is an interesting solvent due to its carbon-carbon double this could be verified with phenol and phenylethers as basically this solvent had high influence on the electropolymerization process [19,20].


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2. Materials and methods

The purities of solvents used (acetonitrile, acetone, ethanol, nitrobenzene, mesityl oxide) were higher than 99% and purity of 1,2,4-benzenetriol was 99% (product of Sigma Aldrich). A 1 mm diameter platinum macro- and a 25 μm diameter platinum microelectrode were used in the studies as working electrodes. A platinum rod counter and silver wire reference electrode were also involved in the three electrode cell and the electrodes were connected to a potentiostat (Dropsens, Spain). Tetrabutyl-ammonium perchlorate (TBAP) was used as supporting electrolyte in all of the studies. The surface of each working electrodes has been prepared by polishing with 1 μm average particle size alumina slurry on a polishing cloth before the experiments and ultrasonicated in a sonicating bath and finally thoroughly washed with deionized water and dried with acetone to remove traces of water. As di- and trihydroxybenzenes are generally susceptible to oxidation, the solutions of hydroxyhydroquinone were freshly prepared before the studies.

3. Results and discussions

In order to assess the electrochemical behaviour of 1,2,4-benzenetriol it was dissolved in different non-aqueous solvents to obtain 20 mM concentration. In Figure 1 the obtained comparative curves are presented and, as it can be seen, they are remarkably different depending on the solvent. In acetone and ethanol only one anodic peak appeared due to the fact that at least one hydroxy group remains after the anodic process facilitating the dissolution of products through hydrogen bonds. In contrary, in acetonitrile two peaks showed up. The possible processes mainly occurring in each solvent are displayed in Scheme 1. Looking on the chemical structure of 1,2,4-benzenetriol we can establish that it can undergo electrooxidation in more reaction pathways in parallel to each other similarly to hydroquinone, catechol and resorcinol. In all these pathways two electrons and two protons are involved except for one of the cases of resorcinol reaction where only one electron is transferred. As showed in the fourth process the oxidation is similar to phenol where the unpaired electron in a free para position is able to form a dimer by coupling to other radical. In the case of 1,3-oxidation the third pathway is more probable and leads to polymer formation due to its two unpaired electron. When it oxidizes in 1,2 and 1,4 positions the charge transfer process is reversible without any fouling. Only if the oxidation occurs in 1,3 position can lead to products being able to deactivate the electrode, as it could be established in case of resorcinol. As a matter of fact, resorcinol can be oxidized at one of the hydroxy groups, as in case of phenol, and the electronic structure of the formed phenoxyl radical changes making it inappropriate for reaction of the other hydroxy group. These radicals combine with each other producing oligomers capable of adsorbing to the electrode surface.

In acetone and ethanol the possible deactivating products can dissolve and this could be verified by the high reproducibility of voltammograms. The only one peak comprises all the three possible pathways, this it is valid in any of the studied solvents. The voltammograms can not differentiate between them, as the process is diffusion controlled and they are only influenced by the substrate and then the products will leave the electrode surface not having impact any more on the peak currents. The diffusion controlled nature of processes of 1,2,4-benzenetriol was verified by studying the dependence of peak currents on the square root of scan rate which was linear (not shown). However there are some differences in the oxidation potentials of the possible pathways but depending on the conditions applied (solvent, concentration). It can seen a typical voltammogram with one well defined peak, this peak is assigned to the process which has the most negative oxidation potential. In case of 1,2,4-benzenetriol predominantly the 1,2- and 1,4-oxidation take place at the potential of anodic peak. On the other hand, the maximum number of electrons transferred is 2 for each pathway.
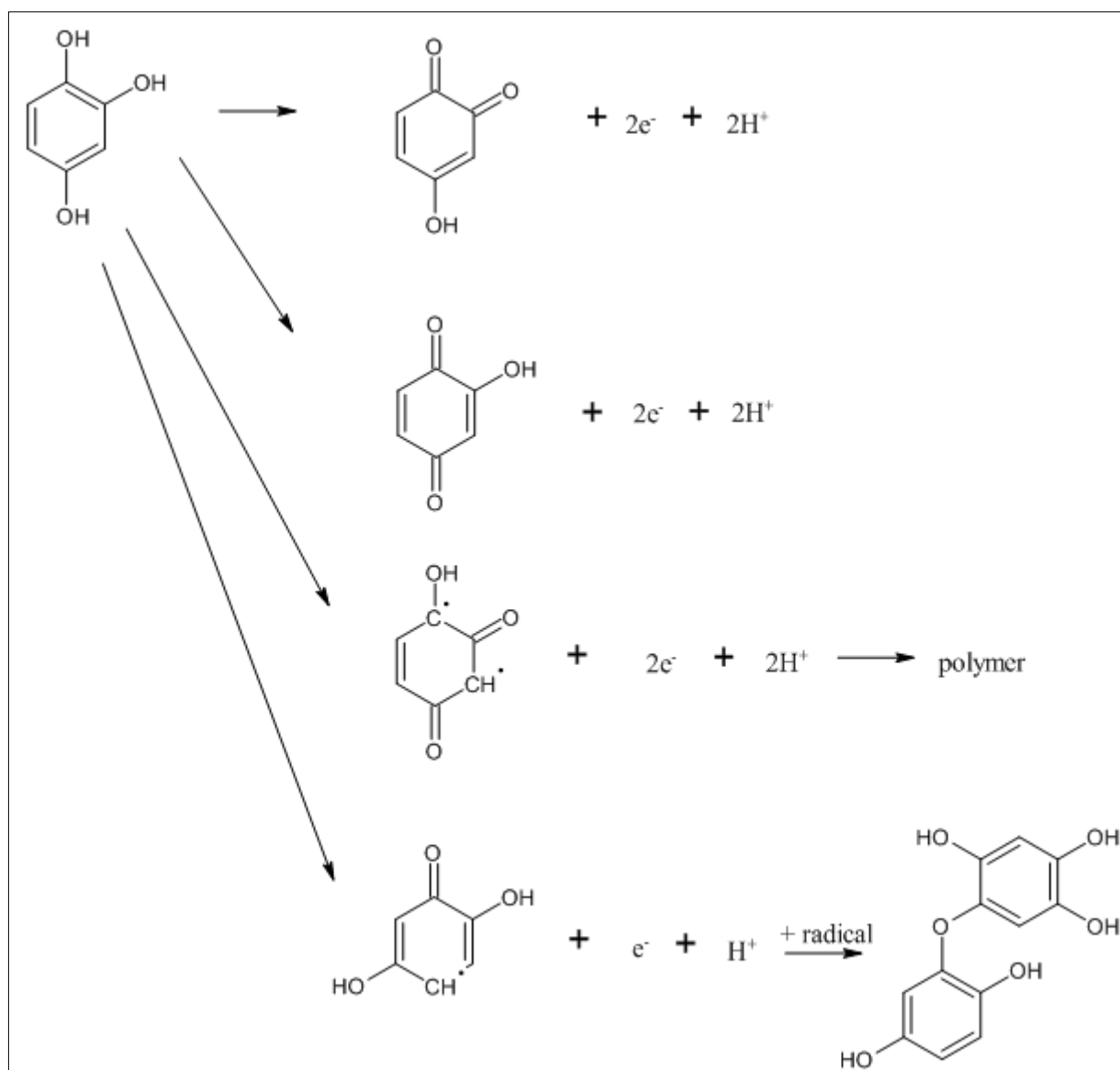
Scheme 1. Possible pathways of 1,2,4-benzenetriol electrooxidation

The double peak in acetonitrile is attributable to a weak deactivation process as oligomeric products arising from 1,3 oxidation are scarcely soluble in it. This hypothesis was verified by investigating the influence of solution concentration on the shape of voltammograms (Figure 2). For 10 mM concentration only one peak appeared indicating that smaller quantity of deactivating products are formed and then fast removal from the electrode surface into the bulk occurred. It is worth mentioning that in case of both 10 and 20 mM concentrations (the latter seen in Figure 1) the reproducibility was acceptable showing that the shape of voltammograms are not significantly affected by the previous measurement in case of the smaller concentrations. However, the peak obtained in 20 mM solution begins splitting into two peaks indicating that the effect of the resorcinol pathway became obvious. For 50 mM concentration already three peaks showed up and all in all the observation of different number of anodic peaks does not show unambiguously three different electrode processes. The scans taken for different concentrations reinforce this hypothesis and they also suggest that the peaks can not be assigned to the different possible pathways. In situations where more separated electrode processes are taking place the number of voltammetric peaks should not be influenced by the concentration and moreover, heights of each peak will be proportional to it. In contrary, in the case of 1,2,4-benzenetriol the number of peaks increase by increasing the concentration.
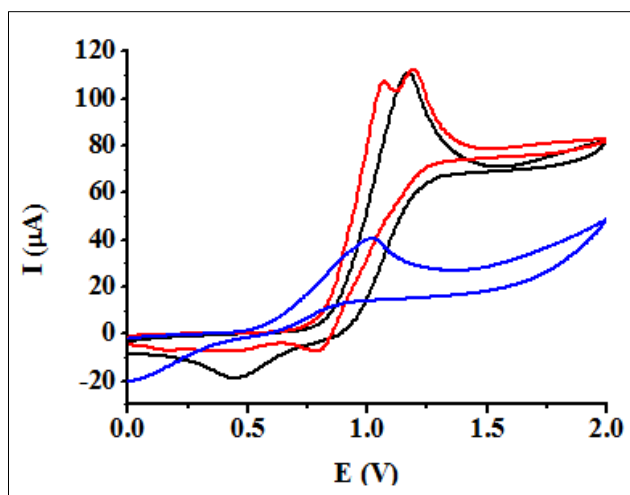
Figure 1. Comparative cyclic voltammetric curves of 20 mM 1,2,4-benzenetriol in acetone (black curve), in acetonitrile (red curve), in ethanol (blue curve) with 1 mm diameter platinum disc (supporting electrolyte 50 mM TBAP, v=0.1 V/s)
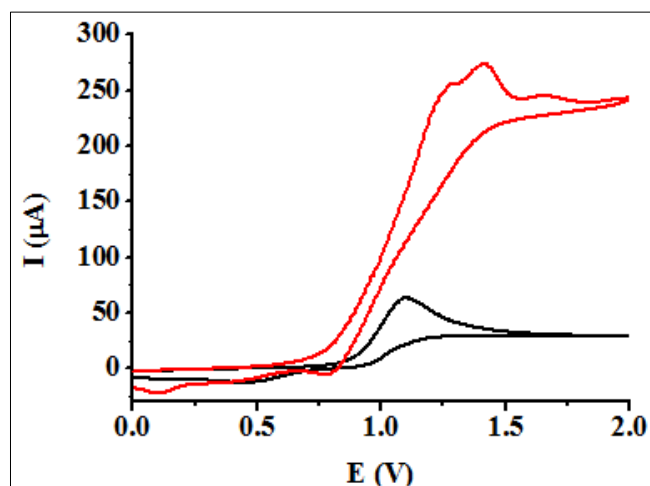

Figure 2. Cyclic Voltammograms of 1,2,4-benzenetriol in acetonitrile for 10 mM (black curve) and 50 mM (red curve) concentration with 1 mm diameter platinum disc (supporting electrolyte 50 mM TBAP, v=0.1 V/s)

The electrooxidation of 1,2,4-benzenetriol was also studied in nitrobenzene and mesityl oxide and some identical behaviour could be noticed (Figure 3). Successive scans were taken in solutions prepared with these solvents as previous studies highlighted that multiple scans might provide interesting results in case of organic compounds being susceptible to formation of radicals during their electrooxidation. In nitrobenzene the height of the second peak of the first scan is remarkably different from that of the other scans. This indicates also a weak deactivation. Previously by investigating pyrogallol in nitrobenzene [17] the repetitive voltammograms showed fast deactivation. However, electrooxidation of pyrogallol has two possible pathways independently on the solvent (oxidation in the 1,2 position and at the middle hydroxy group) the obtained products can be different. Electrochemistry of 1,2,4-benzenetriol is very different from that of pyrogallol in aprotic solvents particularly in nitrobenzene. It also clearly indicates that oxidation occurs predominantly in the 1,2 and 1,4 positions.

The voltammograms in mesityl oxide were almost reproducible suggesting that the participation of solvent is negligible in the charge transfer process (due to the majority of 1,2 and 1,4 dioxo products). In two recent works we showed that due to the carbon-carbon double bond mesityl oxide influences

significantly the electrogenerated polymerization process in case of phenol [19] and phenylethers [20]. These substances have high susceptibility to electrode fouling but studies with hydroquinone and catechol in mesityl oxide revealed the high reproducibility (not shown) so their behaviour resembles to that of 1,2,4-benzenetriol.
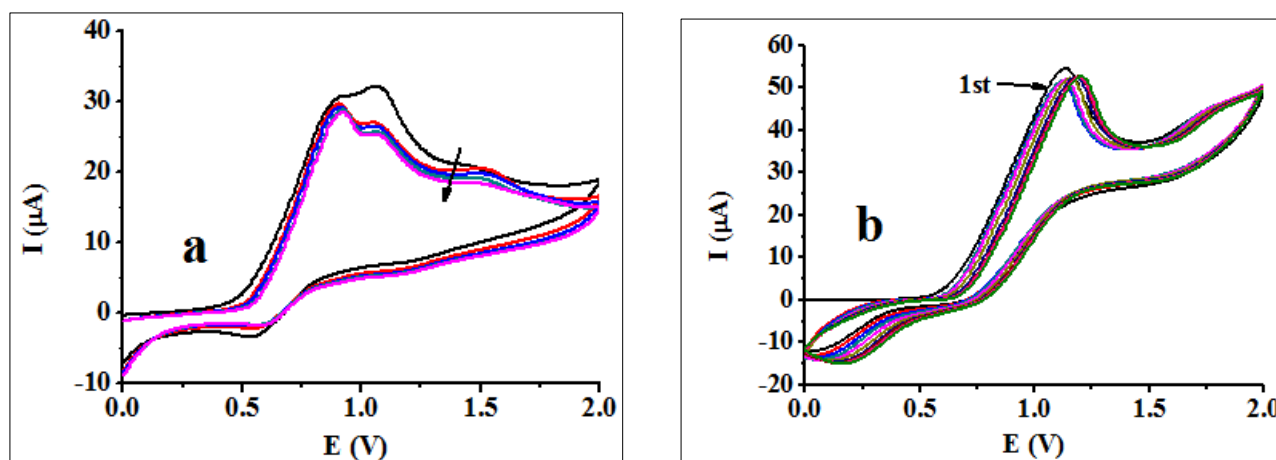

Figure 3. Successive cyclic voltammograms of 20 mM
1,2,4-benzenetriol in nitrobenzene (a) and in mesityl oxide (b) with 1 mm
diameter platinum disc (supporting electrolyte 50 mM TBAP, v=0.1 V/s)

The dependence of anodic peak currents on the concentration of 1,2,4-benzenetriol and electrode size was also studied in acetonitrile. On macroelectrode saturation-like behaviour could be observed which also clearly indicates the weak deactivation (Figure 4a). This was more significant when the electrode was not polished between scans taken in different concentration solutions suggesting that a fraction of polymeric products resist to washing with pure solvent.
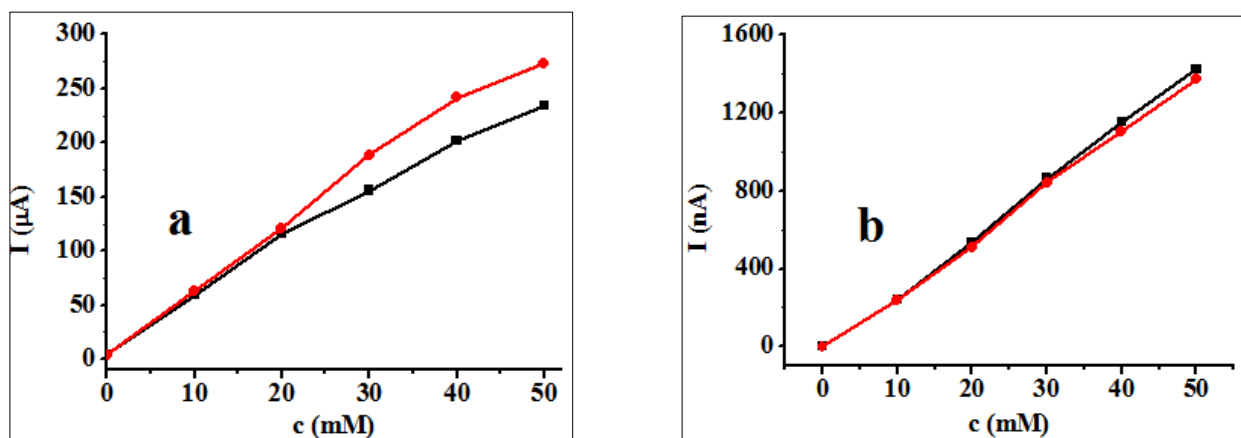

Figure 4. Dependence of current signals on concentration of 1,2,4-benzenetriol on
1 mm diameter platinum macroelectrode (a) and on 25 μm diameter platinum microelectrode (b)
(supporting electrolyte 50 mM TBAP, v=0.1 V/s). Black data points are related
to measurements carried out without polishing between them and red curves reveal the
data for the case when electrode was polished

However, the concentration dependence studies showed some signs of electrode deactivation further studies were carried out with platinum microelectrode (Figure 4b) as generally reduction of electrode size drastically might be susceptible to the presence of blocking materials on its surface. Looking at the related figure a linear dependence of plateau currents on substrate concentration in the same range as

used by macroelectrode experiments could be found. It is in contrast to the general observations with microelectrodes as the formation of blocking products leads to current decline by increasing the concentration. Not this is the case and Figure 5 shows that at 50 mM concentration the first two cycles of the voltammograms are identical and sigmoidal shaped by repeating the scans. The few oligomers formed in these cycles will develop as from the third scan remarkable decline of currents occurs. On the other hand, polishing between measurements in the different concentration solutions has negligible effect on the magnitude of currents as sign of fast removal of the majority of polymeric products due to hemispherical diffusion. It is remarkable on the other hand that distortion of sigmoidal shaped voltammograms to peak shaped ones occurs from the fourth scan indicating the irreversible binding of some polymeric products to the electrode surface which is clearly seen only when scan is repeated in 50 mM concentration solution four times.

The results with microelectrode highlight that on macroelectrode the polymeric products occur in high density leading to stronger adhesion to platinum surface.
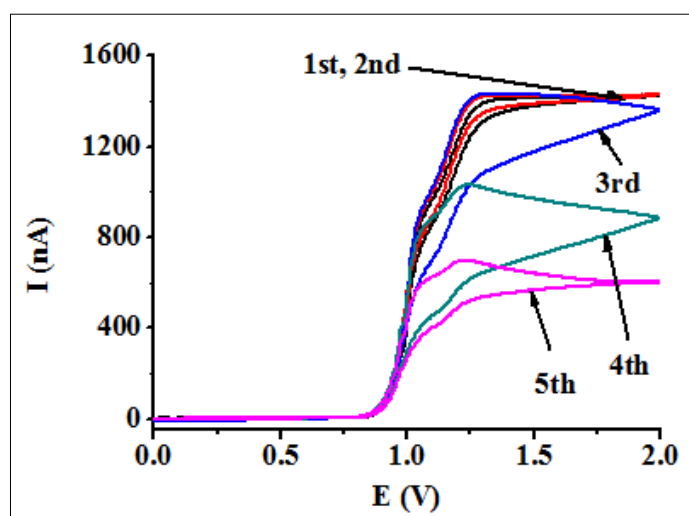

Figure 5 Successive cyclic voltammograms of 50 mM
1,2,4-benzenetriol on 25 μm diameter platinum microelectrode
(supporting electrolyte 50 mM TBAP, *v*=0.1 V/s)

4. Conclusions

The investigations of 1,2,4-benzenetriol in non-aqueous solvents showed that its electrochemical behaviour is identical in the family of polyhydroxy phenols as its electrooxidation can run in different pathways.

The studies aiming to investigate the dependence of the oxidation reaction on electrode size served interesting findings and results with a higher and a smaller surface electrode completed each other. These all showed the existence of 1,3-oxidation. In fact, acetonitrile and nitrobenzene were suitable among the solvents used to prove the latter statement.

The concentration dependence of voltammetric peak currents with using platinum macroelectrode showed nonlinearity attributable to the 1,3-oxidation similarly to resorcinol leading to partial deactivation. Appearance of more peaks indicated the weak deactivation at higher concentrations in acetonitrile and nitrobenzene. At higher concentration the microelectrode became deactivated as in the successive scans the currents declined continuously reinforcing the existence of resorcinol pathway.

The observations encourage the further studies concerning anodic preparation of soluble copolymers in absence of other monomers being more susceptible to fouling for different applications.

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