



Voltammetric Studies of 1,4-dihydroxybenzene and 4-hydroxybenzyl Alcohol Prepared in Aqueous Solutions at Various pH Values

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The electrochemical oxidation of 1,4-dihydroxybenzene and 4-hydroxybenzyl alcohol (4 HBA) in aqueous solutions of different pH values has been studied. The deposition of polymer films on gold electrodes from solutions of 4 HBA was demonstrated by the rapid decrease in current observed in cyclic voltammograms (CVs) subsequent to the first scan. In contrast, no polymer films were formed at the electrode surfaces from solutions of 1,4-dihydroxybenzene regardless of the pH. The eigenvalues for the highest occupied molecular orbitals (HOMO) for both molecules, at all pH values studied, has been calculated and correlated, where possible, with oxidation potentials.

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The electrochemical oxidation of 1,4-dihydroxybenzene, in contrast to what is observed for 1,2-dihydroxybenzene,¹⁻⁴ and 1,3-dihydroxybenzene,⁵⁻⁷ does not usually result in the deposition of insulating polymer layers on electrode surfaces. The observed behavior is often quite complex and demonstrates a dependence on various factors such as pH⁸ but in general the oxidation of 1,4-dihydroxybenzene results in the formation of benzoquinone.⁹ This reaction occurs in protic solvents and involves protonation/deprotonation reactions. This dependence on pH gives rise to the use of the 1,4-dihydroxybenzene/benzoquinone as the basis for a pH electrode.¹⁰

Most studies of the aqueous electrochemistry of 1,4-dihydroxybenzene use buffered solutions. Recently, Chaudhari et al.,¹¹ studied the electrochemistry of 1,4-dihydroxybenzene in unbuffered, neutral aqueous solutions and demonstrated that the behavior is highly complex. In aprotic media (such as acetonitrile) no protons are available so the oxidation products, a semiquinone and a quinone dianion, are different.¹²

The electrochemistry of the related compound 4 HBA has not been studied in aqueous solutions. The behavior of 4 HBA in basic methanol solutions has been studied by Pham et al.,¹³ and they demonstrated that the electrochemical oxidation of 4 HBA leads to the deposition of polymers films on the electrode surface.

The electrochemical behavior of 4 HBA is compared to that of 1,4-dihydroxybenzene and a link is made between oxidation potentials, pKa and the energy of the highest occupied molecular orbital (HOMO) of the molecules in different states of ionization.

The main focus of the paper is to study the electropolymerization of 4-hydroxybenzyl alcohol in aqueous solutions. 1,4-dihydroxybenzene has received some attention in the past and it is specifically studied at neutral pH in unbuffered solutions.¹¹ The study of 1,4-dihydroxybenzene in this paper is really to serve as a contrast to the behavior of 4-hydroxybenzyl alcohol. Hence the 1,4-dihydroxybenzene compound has been studied at the same potential range as 4-hydroxybenzyl alcohol.

Experimental

All chemicals were analytical grade and used without further purification. 4-hydroxybenzyl alcohol (4 HBA) (98%), 1,4-dihydroxybenzene (99%), potassium chloride (99%), potassium ferrocyanide trihydrate (>98%), potassium ferricyanide (>98%) were all procured from Alfa Aesar. Sodium hydroxide (98%) and sulfuric acid (95–98%) were purchased from PRS, Panreac, Spain.

All electrochemical experiments were carried out in a three-electrode glass cell. An EZstat Pro potentiostat (NuVant Systems Inc., IN, USA) equipped with an EZware 2013 V7 was used throughout the

course of the work. Before each cyclic voltammetry (CV) experiment, the gold working electrode was polished mechanically for 2 min using 0.05 μm alumina on polishing pads (PK-4 polishing kit, BASi, IN, USA). This was followed by flushing the electrode surface with deionized water for a few minutes, in order to remove any residual alumina. The polished electrode was then electrochemically tested using a solution of 5 mmol L⁻¹ ferri/ferro cyanide containing 100 mmol L⁻¹ potassium chloride between -0.2 V and 0.6 V vs. Ag/AgCl (3.0 mol L⁻¹ KCl) at sweep rate of 20 mV s⁻¹ for 2 sweeps of potential.

4 HBA and 1,4-dihydroxybenzene were electrochemically oxidized at 1.6 mm diameter gold electrodes. Neutral, acidic and basic solutions of 100 mmol L⁻¹ 4 HBA and 5 mmol L⁻¹ 1,4-dihydroxybenzene were prepared using either potassium chloride (100 mmol L⁻¹ M), sulfuric acid (100 mmol L⁻¹) or sodium hydroxide (100 mmol L⁻¹) as the supporting electrolyte. The electrochemistry of said solutions was studied by sweeping the potential of the working electrode between 0 V and 1 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl, at various sweep rates (5, 10 and 20 mmol L⁻¹ V s⁻¹) for 5 sweeps of potential. The counter electrode was a 230 mm coiled platinum wire mounted in a CTFE cylinder. All electrodes were manufactured by BASi Pre-clinical Services, IN, USA. After the polymerization stage, a cyclic voltammetry run was conducted in ferri/ferro cyanide solution to insure that the film formation was achieved and this was done at the same settings as mentioned previously.

The frontier molecular orbital energies of the HOMO and the Lowest Unoccupied Molecular Orbital (LUMO) for the compounds under study here have been calculated using the Spartan 14 V1.1.4 molecular modelling suite package on a personal computer. For all neutral and ionic structures built, the geometry optimization and calculation of other parameters at the ground state were performed at restricted Hartree-Fock (RHF) level using 3-21G*, 6-31G* and 6-311G* basis sets in order to compare the effects of different basis sets on the calculated electronic properties of the systems. It was found that the HF/6-311G* calculated energy values were the smallest among all the calculated values for other basis systems, therefore this system was considered in the presented study.

Results and Discussion

The compound 1,4-dihydroxybenzene has two pKa values which are 9.85 and 11.40.¹⁴ In acidic solutions the molecule is uncharged and at a pH of 9.85 the monovalent ion and neutral molecule are present at equal concentration. At pH 11.4 the monovalent and divalent anions have equal concentrations and it is clear that the chemical species that are electrochemically oxidized depends on the pH of the solution.

The compound 4 HBA has only one pKa value which is 9.82.¹⁵ The hydroxyl group which is not bonded directly to the benzene ring has properties comparable to those of benzyl alcohol, an aromatic

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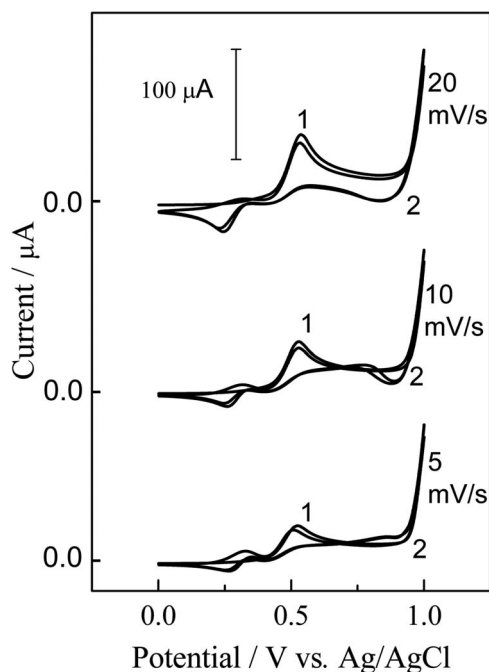


Figure 1. The oxidation and reduction of 5 mmol L⁻¹ 1,4-dihydroxybenzene at neutral pH using a gold working electrode with a diameter of 1.6 mm at various sweep rates. The first two CVs for each sweep rate are shown.

compound with a pKa in excess of 15. It follows that the compound is first ionized via the hydroxyl group on the benzene ring. This phenoxide ion is stabilized by resonance interaction of the negative charge with the carbon atoms on the benzene ring.

The potentials at which redox reactions of chemical species in solution occur are determined by the energy of the HOMO relative to the energy of the electrons in the Fermi level of the electrode. The energy of the HOMO is typically correlated with the oxidation potential such that the oxidation potential becomes progressively more anodic as the energy of the HOMO decreases.

Ideally both compounds (1,4-dihydroxybenzene and 4-hydroxybenzyl alcohol) would have been studied at a concentration of 100 mmol L⁻¹. However, it was found that the currents for oxidation and reduction of 1,4-dihydroxybenzene in neutral and acid solutions at 100 mmol L⁻¹ are too large to be measured by the potentiostat. Therefore the oxidation and reduction of 1,4-dihydroxybenzene was studied at lower concentrations. For the sake of consistency we used a concentration of 5 mmol L⁻¹ in basic solutions also, even though the currents are much smaller.

Figure 1 shows the cyclic voltammograms for the oxidation of 1,4-dihydroxybenzene at neutral pH in unbuffered solutions. The behavior is complex. The behavior of 1,4-dihydroxybenzene at such conditions has been studied by Chaudhari et al.¹¹ They note three major anodic peaks (at 0.73, 0.426 and -0.05 V vs Ag/AgCl) and two cathodic peaks (at 0.25 and -0.17 V vs. Ag/AgCl). They found that the peaks at 0.73 V and -0.17 V were most prominent on the first sweep and that the height of the other peaks grew (at the expense of the peaks at 0.73 V and 0.25 V) as the number of cycles increased. They found that the cyclic voltammograms became self-similar after 10 cycles.

Such complex behavior has not been observed in this study. One major anodic peak is observed at 0.6 V vs. Ag/AgCl, 3.0 mmol L⁻¹ KCl (with perhaps a smaller anodic peak at 0.3 V) and one major cathodic peak at 0.25 V vs. Ag/AgCl, 3.0 mmol L⁻¹ KCl. These peaks presumably correspond to the redox reactions of the 1,4-dihydroxybenzene/benzoquinone couple. It is clear that no polymer is formed at the electrode surface as the currents observed do not decrease appreciably upon repeated potential cycling.

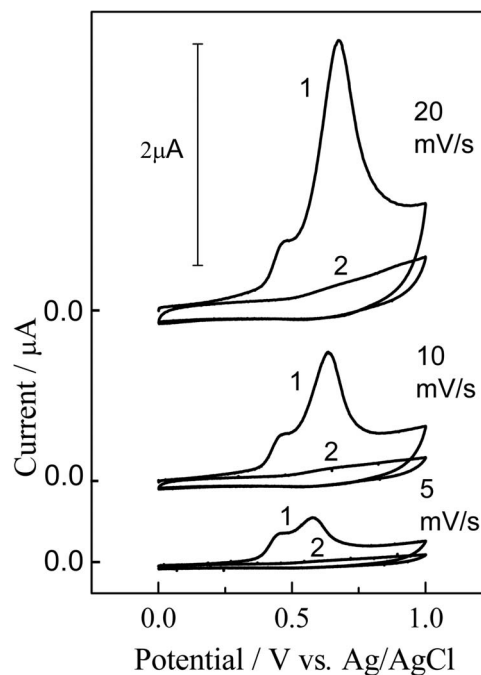


Figure 2. The oxidation and polymerization of 100 mmol L⁻¹ 4 HBA at neutral pH using a gold working electrode with a diameter of 1.6 mm at various sweep rates. The first two CVs for each sweep rate are shown.

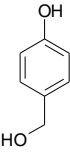
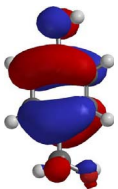
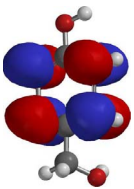
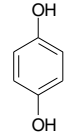
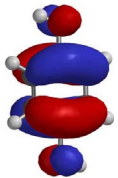
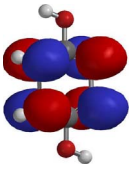
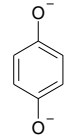
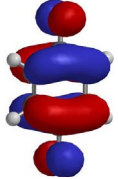
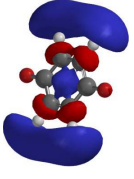
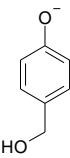
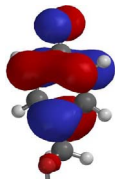
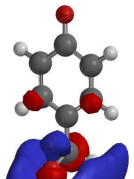
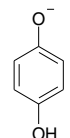
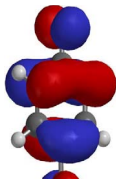

In contrast the cyclic voltammograms for the oxidation of 4 HBA in neutral solutions, shown in Figure 2, demonstrate the formation of a polymer as the currents clearly decrease on cycles subsequent to the first. The polymer is formed through radical intermediates. The onset and peak potentials for oxidation and polymerization are approximately 0.4 and 0.7 V vs. Ag/AgCl, 3.0 mmol L⁻¹ KCl. The energies of the HOMOs of the uncharged molecules (predominant at neutral pH), shown in Table 1, are very similar. When comparing both molecules it is clear that the formation of the stable benzoquinone molecule, upon the oxidation of 1,4-dihydroxybenzene, provides more insight into the difference in observed behavior.

Gattrell and Kirk,¹⁶ have established the mechanism for the electrochemical oxidation and subsequent polymerization of hydroxybenzene (phenol). They posit that radicals are formed through the removal of an electron from a lone pair on the oxygen atom and that, in the pH range below the pKa of phenol, the hydrogen atom on the oxygen atom is then lost. They also posit that monomers with phenol functionality are more prone to dimerization more through carbon-carbon coupling of aromatic rings than through carbon-oxygen coupling provided that such coupling is not sterically hindered.¹⁶ Such carbon-carbon linked dimers react further to form oligomers and ultimately insulating polymer layers with monomer concentration, electrode material, reactant adsorption characteristics, pH, current density and voltage all being important in determining what reaction pathway is followed. It is expected that 4 HBA will follow similar reaction pathways to phenol and the reactions are outlined in Figure 3.

The radical formed is stabilized through resonance structures that distributes the electron density around the benzene ring. The dimers formed are further oxidized (in a similar fashion to the monomer) to form oligomers and eventually a polymer that deposits on the electrode surface.

The potentials for the oxidation and polymerization of 4 HBA in 0.1 mol L⁻¹ sulfuric acid (the solution pH being 0.5) are shifted anodically (see Figure 4). It is more difficult to oxidise and polymerize the compound in acidic solutions. A great number of chemical and electrochemical reactions occur when phenols are electrochemically oxidized complicating the analysis of the data. It is therefore not clear if the loss of hydrogen occurs simultaneously with (wherein

Table I. Molecular structure, eigenvalues for HOMO and LUMO molecular orbitals and electron density distribution for 1,4-dihydroxybenzene, 4-hydroxybenzyl alcohol and their ionized forms. All values were calculated using the Spartan 14 V1.1.4 molecular modelling suite package.

		E_HOMO / eV	HOMO Plots	E_LUMO / eV	LUMO Plots
A		-8.5		3.4	
B		-8.0		3.4	
C		3.6		12.5	
D		-2.1		7.0	
E		-1.7		7.5	

the oxidation potentials would be a function of pH as described by the Nernst equation) or post oxidation of the compound. The shift in potentials might be explained by noting the already high concentration of hydronium ions in acidic solutions that could act to retard the dimerization and polymerization reactions as such reactions require the loss of protons from the oxidized molecules.

In contrast the behavior of 1,4-dihydroxybenzene in 0.1 mol L⁻¹ sulfuric acid (pH 0.3), shown in Figure 5, is that of a classic redox couple. An anodic peak can be seen at about 0.425 V vs. Ag/AgCl, 3.0 mmol L⁻¹ KCl and a cathodic peak is apparent at 0.375 V vs. Ag/AgCl, 3.0 mmol L⁻¹ KCl. In contrast phenol will polymerize at this pH.¹⁷ The behavior is more similar to that which would be expected in buffered solutions. This can be explained by noting that the amount of acid generated by the electrochemical reactions would be very small and insufficient to significantly perturb the concentration of acid solutions. In contrast the behavior of 1,4-dihydroxybenzene in 0.1 mol L⁻¹ sodium hydroxide (pH 13.4) is unusual.

The cyclic voltammograms are shown in Figure 6 and there is no distinct anodic peak. 1,4-dihydroxybenzene exists as a divalent anion at this pH. A peak can be seen at 0.2 V vs. Ag/AgCl, 3.0 mmol L⁻¹

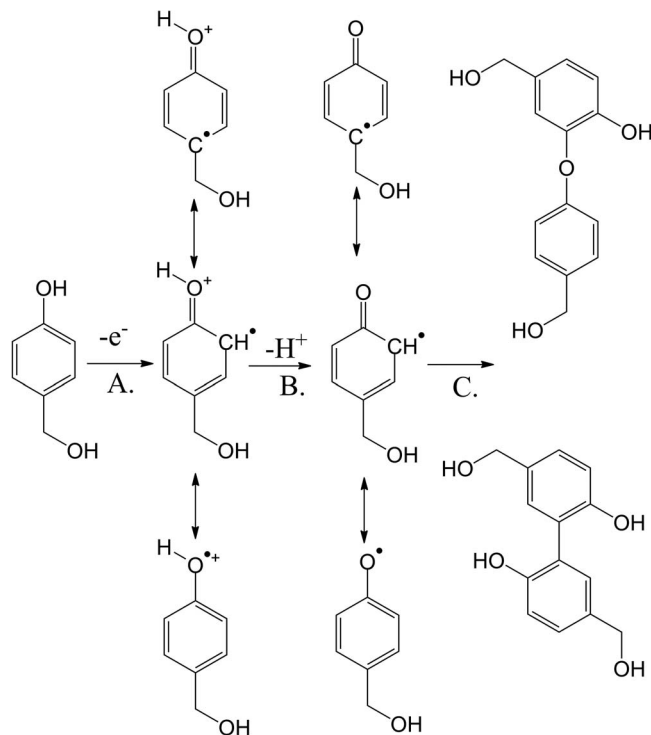


Figure 3. A schematic for the anodic oxidation and polymerization of 4 HBA.

KCl but this cannot be classed as a cathodic peak because no cathodic currents are observed.

The pH of the basic solutions from which 4 HBA was polymerized was 11.6 and at this pH 4 HBA exists in an ionized form. The energy of the HOMO of the ionized form of 4 HBA is much lower than the unionized form. Based on the theory the oxidation and polymerization of 4 HBA from alkaline solutions would be easier than from neutral

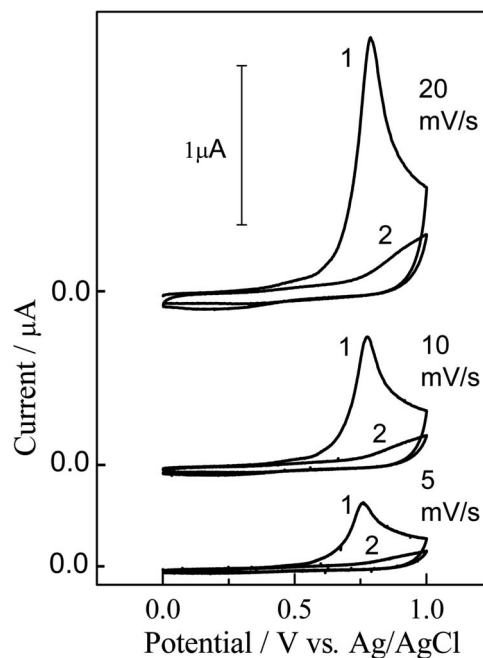


Figure 4. The oxidation and polymerization of 100 mmol L⁻¹ 4 HBA in acidic solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates. The first two CVs for each sweep rate are shown.

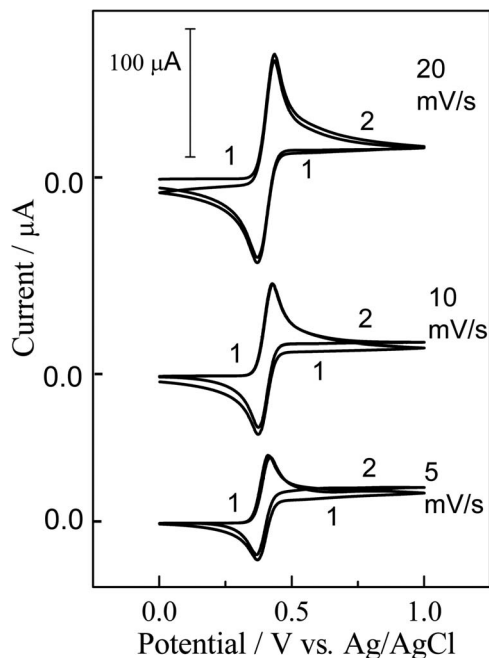


Figure 5. Oxidation and reduction of 5 mmol L⁻¹ 1,4-dihydroxybenzene in acidic solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates. The first two CVs for each sweep rate are shown.

and acidic solutions versus a pH insensitive reference electrode. This is shown in Figure 7 where the potentials at which oxidation and polymerization occurs in alkaline solutions are much lower than for acidic (a difference in peak potential of circa 0.45 V) and neutral (a difference in peak potential of circa 0.3 volts) solutions.

Conclusive proof of the presence of a polymer film on the electrode surface is shown in Figure 8. Figure 8A presents a typical cyclic voltammogram run of a gold electrode after mechanical polishing with

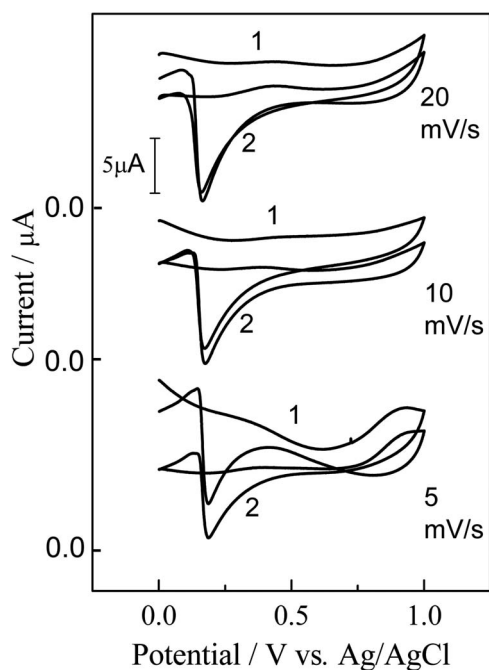


Figure 6. Oxidation and reduction of 5 mmol L⁻¹ 1,4-dihydroxybenzene in basic solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates. The first two CVs for each sweep rate are shown.

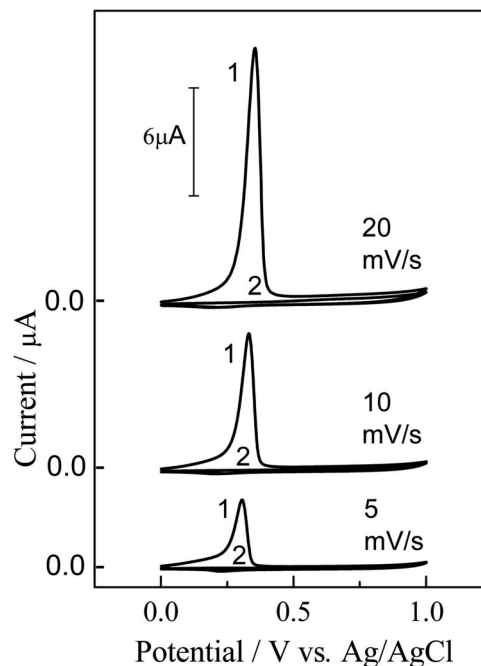


Figure 7. Oxidation and polymerization of 100 mmol L⁻¹ 4 HBA in basic solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates. The first two CVs for each sweep rate are shown.

a slurry of 0.05 μm alumina powder. After the polishing stage the electrode was immediately tested in a 5 mmol L⁻¹ ferri/ferro cyanide solution containing 100 mmol L⁻¹ KCl supporting electrolyte. In contrast, Figure 8B presents a typical cyclic voltammogram run of the same gold electrode tested in the same solution after electropolymerization of 4 HBA from a basic solution. It can be clearly seen that the current is dropped sharply into the nanoamp range and the smooth peaks feature has totally disappeared from the scans.

The oxidation and dimerization reactions of 4 HBA in alkaline solutions are shown in Figure 9. Given that the monomer is already ionized, protons are no longer lost from the compound as a consequence of oxidation. The dimers formed are ultimately negatively charged due to the alkaline nature of their environment.

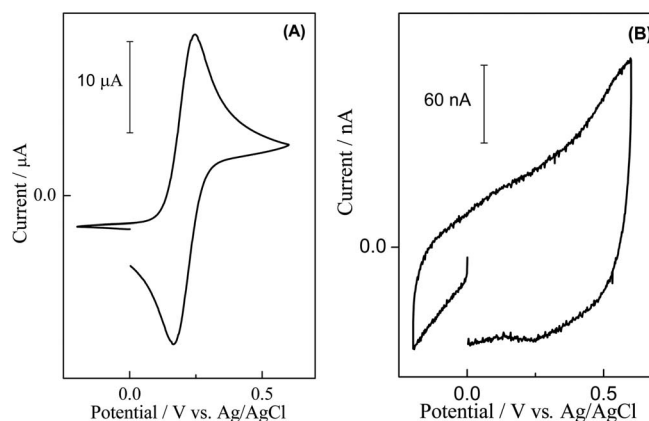


Figure 8. (A) A typical cyclic voltammogram run of polished gold electrode tested in 5 mmol L⁻¹ ferri/ferro cyanide 100 mmol L⁻¹ KCl solution (before polymerization), (B) A typical cyclic voltammogram run of the same gold electrode after the polymerization from a solution of 4 HBA in 100 mmol L⁻¹ sodium hydroxide.

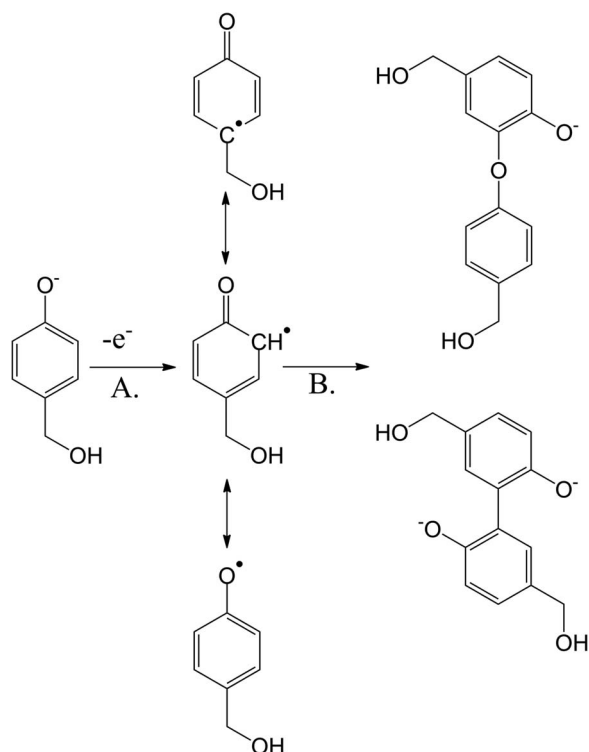


Figure 9. A schematic for the oxidation and polymerization of 4 HBA in base.

Conclusions

The electrochemical oxidation behavior of 1,4-dihydroxybenzene and 4 HBA is very different. In neutral, acidic and basic solutions

the anodic oxidation of 4 HBA results in the formation of insulating polymers at the electrode surface. In contrast the oxidation of 1,4-dihydroxybenzene does not result in polymer deposition. Instead redox type behavior is observed instead.

Acknowledgments

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