

## A Study of the Electrochemical Oxidation and Polymerisation of 1,3 dihydroxybenzene and 3-hydroxybenzyl alcohol in Acidic, Basic and Neutral Aqueous Solutions

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The electrochemical oxidation and polymerisation of 1,3 dihydroxybenzene (resorcinol) and 3-hydroxybenzyl alcohol (3HBA) from aqueous neutral, acidic and basic solutions is studied. The development of polymer films on the electrodes is confirmed by the rapid decrease in current seen in the cyclic voltammograms (CV). The currents in alkaline solutions are much higher than in acidic or neutral solutions. It is more difficult to oxidise and polymerise both compounds in acidic solutions. The currents associated with the oxidation and polymerisation of resorcinol were found to be higher than for the 3HBA in all tested media. The optimised structures of the molecules and the frontier molecular orbital energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of each compound and derived anions are calculated. All values have been carried out by restricted Hartree–Fock (RHF) level using 6-311G\* basis set. The calculated energy levels are used to explain the observed electrochemical behaviour.

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**Keywords:** Voltammetry; Electropolymerization; Oxidation; HOMO; LUMO; RHF

### 1. INTRODUCTION

The electrochemical polymerisation of 1,3 dihydroxybenzene has received scant attention in the literature. Kennedy et al [1] have studied the polymerisation of 1,3 dihydroxybenzene from neutral and acidic solutions in a study also comprising the study of 3-aminophenol and 1,3-phenylenediamine. They concluded that insulating polymer films of nanometre thickness are deposited as a result of the

anodic oxidation of 1,3 dihydroxybenzene. Kennedy and Cunnane [2] further demonstrated that such films could be modified through exposure to caustic solutions to form microelectrode ensembles.

The electrochemical copolymerisation of 1,3 dihydroxybenzene and 1,3- phenylenediamine for biosensor applications has been investigated. Geise et al [3, 4] looked at various electropolymerised films at several electrodes and concluded that a film of poly (1,3-phenylenediamine-co-1,3 dihydroxybenzene) gave the best stability and protection. Carelli et al. [5] investigated various dihydroxybenzenes in their study of interference free biosensors.

Bassi et al. [6] immobilised the enzyme fructose dehydrogenase behind a non-conducting film of poly (1,3-phenylenediamine-co-1,3 dihydroxybenzene) so as to create a fructose biosensor. In the same year Park and co-workers [7] published a paper on a polymer-coated, carbon fibre nitric oxide sensor. They found that a coating of a composite polymer generated from nafion, 1,3-phenylenediamine and 1,3 dihydroxybenzene gave the best results. Pontie et al. [8] came to similar conclusions in their 1999 paper.

More recently Enache et al [9] have studied the oxidation of 1,3 dihydroxybenzene using differential pulse voltammetry and conclude that such oxidation reactions are irreversible. Dong [10] has studied the oxidation of 1,3 dihydroxybenzene at modified glassy carbon electrodes and found that gold nanoparticle/carbon nanotube modified glassy carbon electrodes are promising for detecting 1,3 dihydroxybenzene. Wang et al [11] used modified graphene electrodes for the determination of 1,3 dihydroxybenzene.

Pham et al [12] studied the oxidation and polymerisation of 3-hydroxybenzyl alcohol in a basic methanol solution and obtained thin polymer films; one of the few electrochemical studies of this compound. In this paper we will compare and contrast the electrochemical behaviour of 3-hydroxybenzyl alcohol with that of 1,3 dihydroxybenzene and make the link between oxidation potentials, pKa and the energy of the highest occupied molecular orbital (HOMO) of the molecules in different states of ionisation.

## 2. EXPERIMENTAL PART

### 2.1 Chemicals

All chemicals were analytical grade and used without further purification. 3-hydroxybenzyl alcohol (3HBA) (98%), 1,3 dihydroxybenzene (99%), potassium chloride (99%), potassium ferrocyanide trihydrate (>98%), potassium ferricyanide (>98%) were all procured from Alfa Aesar. Sodium hydroxide (98%) and Sulphuric acid (95-98%) were purchased from PRS, Panreac Spain.

### 2.1 Film Preparation

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) run, the gold working electrode was

polished mechanically for 2 min using 0.05 $\mu$ m Alumina polishes and the polishing pads of the PK-4 polishing kit (BASi, IN, USA). This was followed by flushing with deionised water for a few minutes, in order to remove any residual alumina. The polished electrode was then electrochemically tested using a solution of 5 mM ferri/ferro cyanide containing 100 mM potassium chloride between -0.2 V and 0.6 V vs. Ag/AgCl at sweep rate of 20 mV s<sup>-1</sup> for 2 sweeps of potential.

3HBA and 1,3 dihydroxybenzene were then oxidatively electropolymerised onto 1.6 mm gold electrodes. Concentrations of 100 mM 3HBA or 1,3 dihydroxybenzene were prepared from neutral (100 mM potassium chloride), acidic (100 mM sulphuric acid) or basic solutions (100 mM sodium hydroxide) by sweeping the potential of the working electrode between 0 V and 1 V vs. Ag/AgCl at various sweep rates (5, 10 and 20 mV s<sup>-1</sup>) for 5 sweeps of potential. The counter electrode was 230 mm coiled platinum wire mounted in a CTFE cylinder. All electrodes were manufactured by BASi Preclinical Services, IN, USA. After the polymerisation stage, a cyclic voltammetry run was conducted in ferri/ferro cyanide solution to insure that the film formation was achieved; this was done as same settings as mentioned above.

## 2.2 Molecular Orbital Calculations

The frontier molecular orbital energies of the Highest Occupied Molecular Orbital (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 [1]. For all neutral and ionic proposed 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 set in order to compare the effects of different basis sets on the 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.

## 3. RESULTS AND DISCUSSIONS

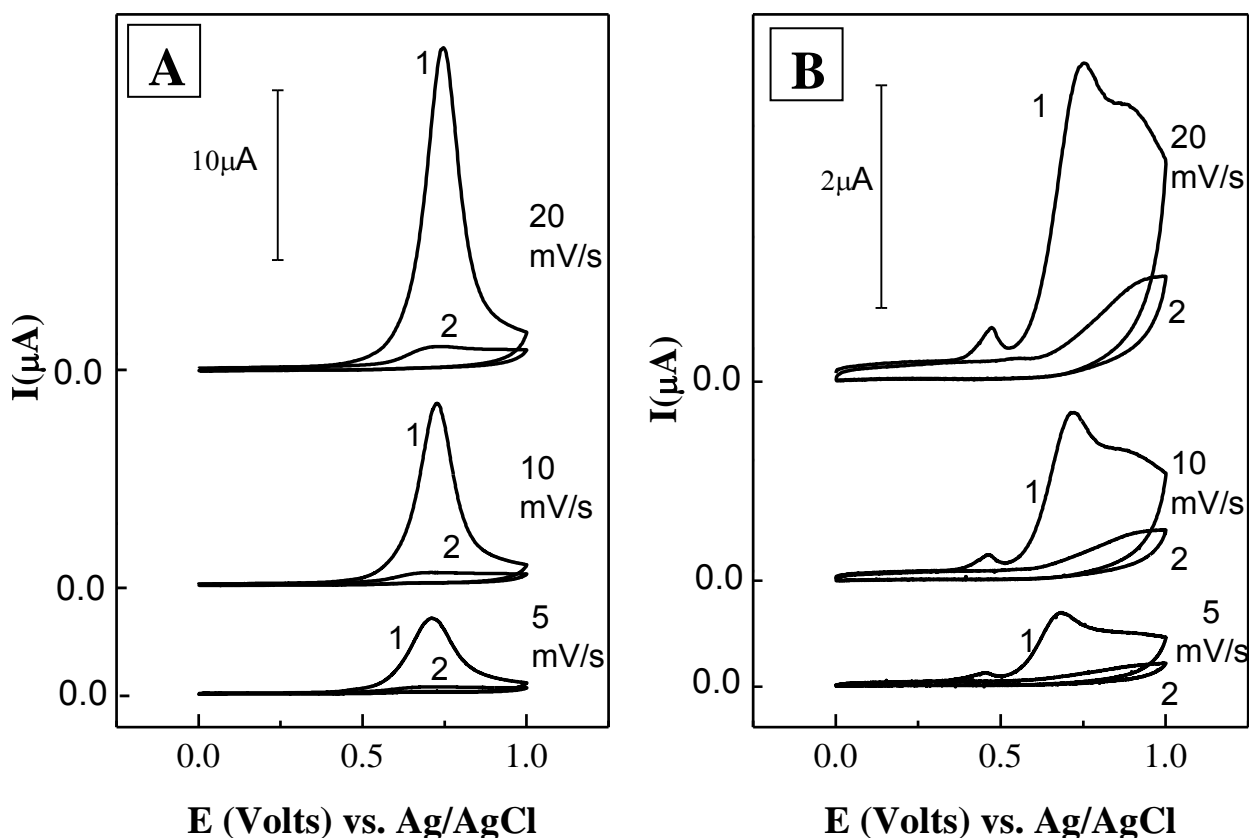
Phenol is a simple aromatic compound with a pKa of 9.99 [13] wherein the hydroxyl group is directly bonded to a carbon atom on the benzene ring. Benzyl alcohol is also an aromatic compound but it has a pKa in excess of 15. The pKa of phenol is much lower than that of benzyl alcohol as the phenoxide ion is stabilised by the resonance interaction of the negative charge with the carbon atoms on the benzene ring. Such resonance interaction is not possible for the anion of benzyl alcohol and thus it has a pKa similar to that of simple aliphatic alcohols.

The meta orientation of the hydroxyl groups of 1,3 dihydroxybenzene does not allow for resonance interaction of the functional groups and 1,3 dihydroxybenzene has certain properties that are very similar to those of phenol. Kennedy et al demonstrated that the calculated energy of the highest occupied molecular orbital (HOMO) of 1,3 dihydroxybenzene is close to that of phenol, while the

energy of the HOMO of the para isomer hydroquinone (where resonance is possible) was shown to be different.

Similarly the meta orientation and nature of the functional groups of 3-hydroxybenzyl alcohol precludes there being resonance interaction between the functional groups. Consequently 3-hydroxybenzyl alcohol has a pKa similar to that of phenol and only a monovalent anion is formed in alkaline solutions as the benzyl alcohol moiety does not ionise below pH 14. In contrast 1,3 dihydroxybenzene forms both a monovalent ion (near pH 9.4) and a divalent anion (near pH 10.9).

Oxidation of a species in solution occurs at an electrode when the electrode potential is raised such that electrons can be accepted from the HOMO of species in solution. Therefore chemical species with HOMOs of similar energy can be expected to have similar oxidation potentials. Cyclic voltammograms for the oxidation and polymerisation of 1,3 dihydroxybenzene and 3-hydroxybenzyl alcohol in neutral solutions are shown in Fig. 1A and 1B, respectively. The onset and peak potentials for oxidation and polymerisation are very similar for both compounds, explained by the similarity in the calculated HOMO values shown in Table 1.



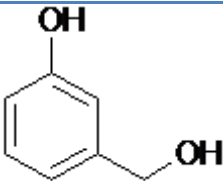
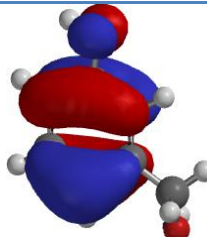
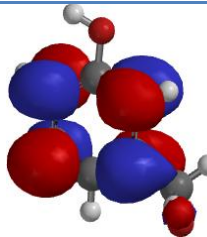
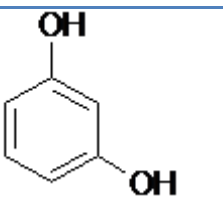
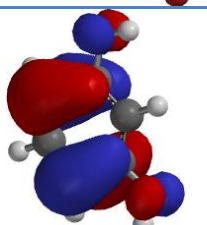
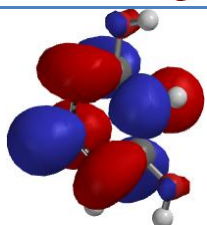
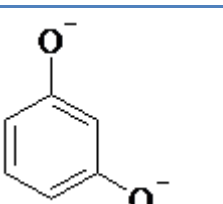
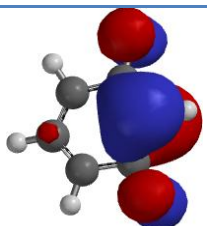
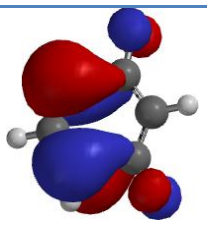
**Figure 1.** Cyclic voltammograms for the oxidation and polymerisation from neutral solutions of (A) 1,3 dihydroxybenzene, and (B) 3-hydroxybenzyl alcohol.

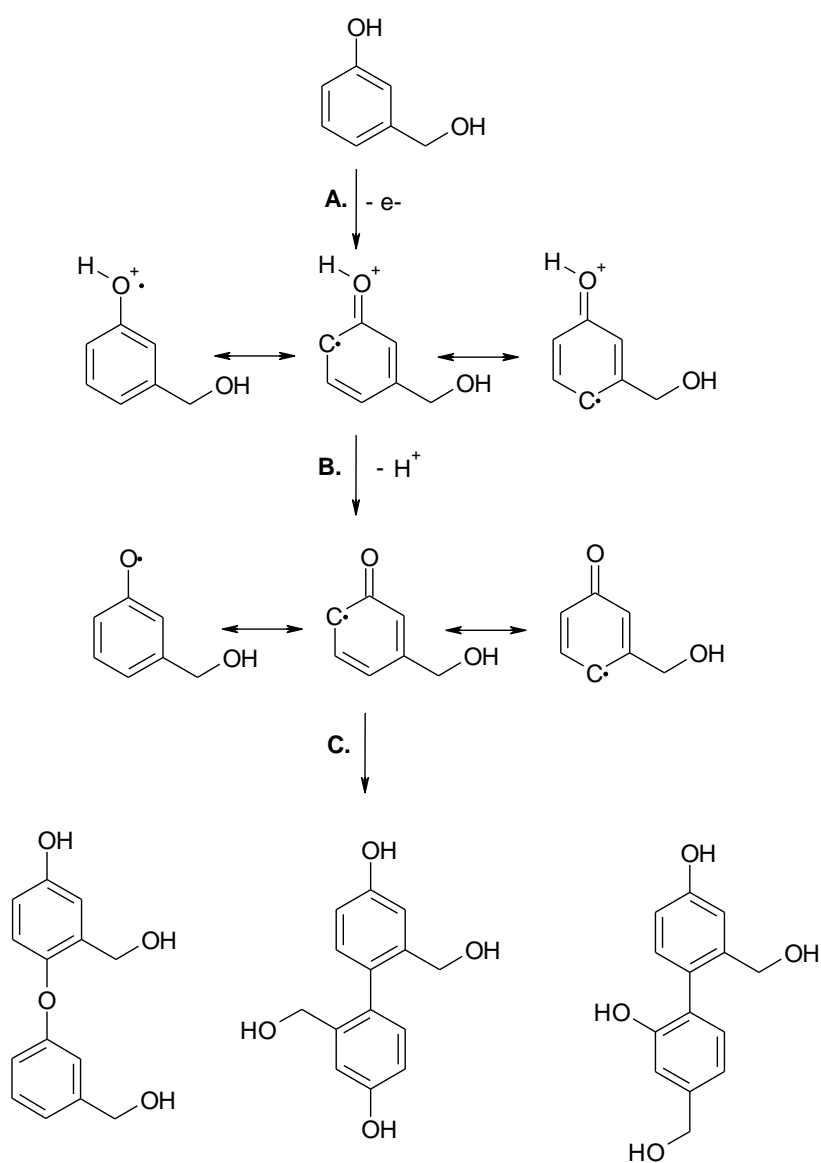
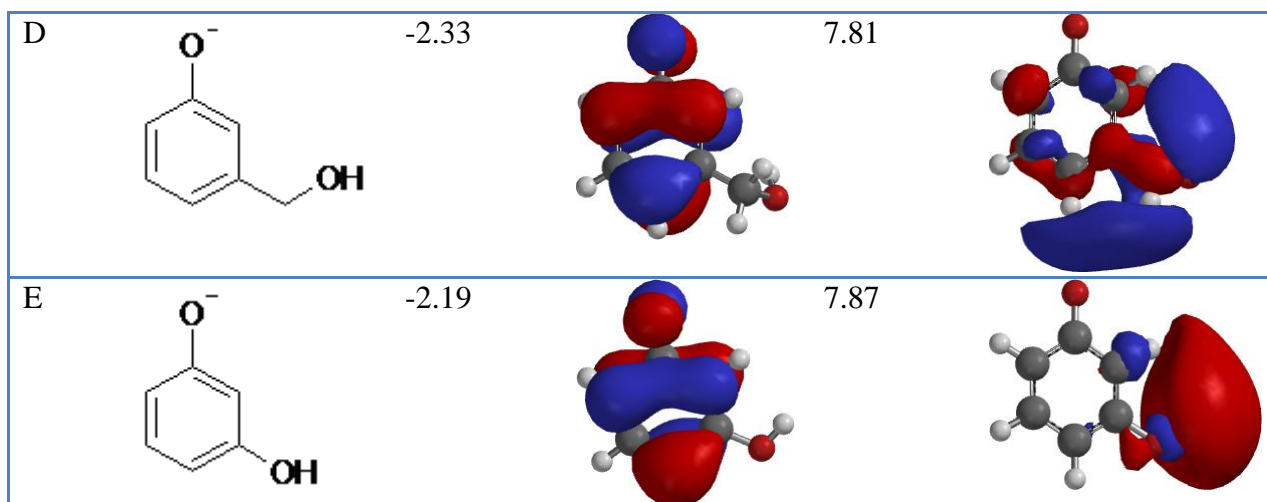
The currents associated with the oxidation and polymerisation of 1,3 dihydroxybenzene are higher than for the 3-hydroxybenzyl alcohol indicating that poly 1,3 dihydroxybenzene forms thicker films than poly 3-hydroxybenzyl alcohol. The presence of polymer films is confirmed by the rapid decrease in current scans seen subsequent to the first.

Gattrell and Kirk [14] proposed a mechanism for the electrochemical oxidation, dimerization and subsequent polymerisation of phenol and Kennedy et al described the equivalent reactions for 1,3 dihydroxybenzene. Gattrell and Kirk postulate that radicals are formed through removal of an electron from a lone pair on the oxygen atom. In the pH range below the pKa of phenol this is then followed by the loss of the hydrogen atom on the oxygen atom. These radicals are stabilised through resonance interaction with the benzene ring.

Gattrell and Kirk showed that as phenol monomers become less sterically hindered polymerisation tends to occur more through the carbon-carbon coupling of aromatic rings than through carbon-oxygen coupling. The carbon-carbon linked dimers are free to polymerise through the hydroxyl group leading to a highly cross-linked insoluble polymer. The added caveat is that phenol concentration, electrode material, reactant adsorption characteristics, pH, current density and voltage all play their part in determining what reaction pathway is followed. The monomer 3-hydroxybenzyl alcohol will behave in a similar fashion and the reactions are outlined in Fig. 2. The radical formed is stabilised through resonance structures that distributes the electron density around the benzene ring. The dimers formed are further oxidised (in a similar fashion to the monomer) to form oligomers and eventually a polymer that deposits on the electrode surface.

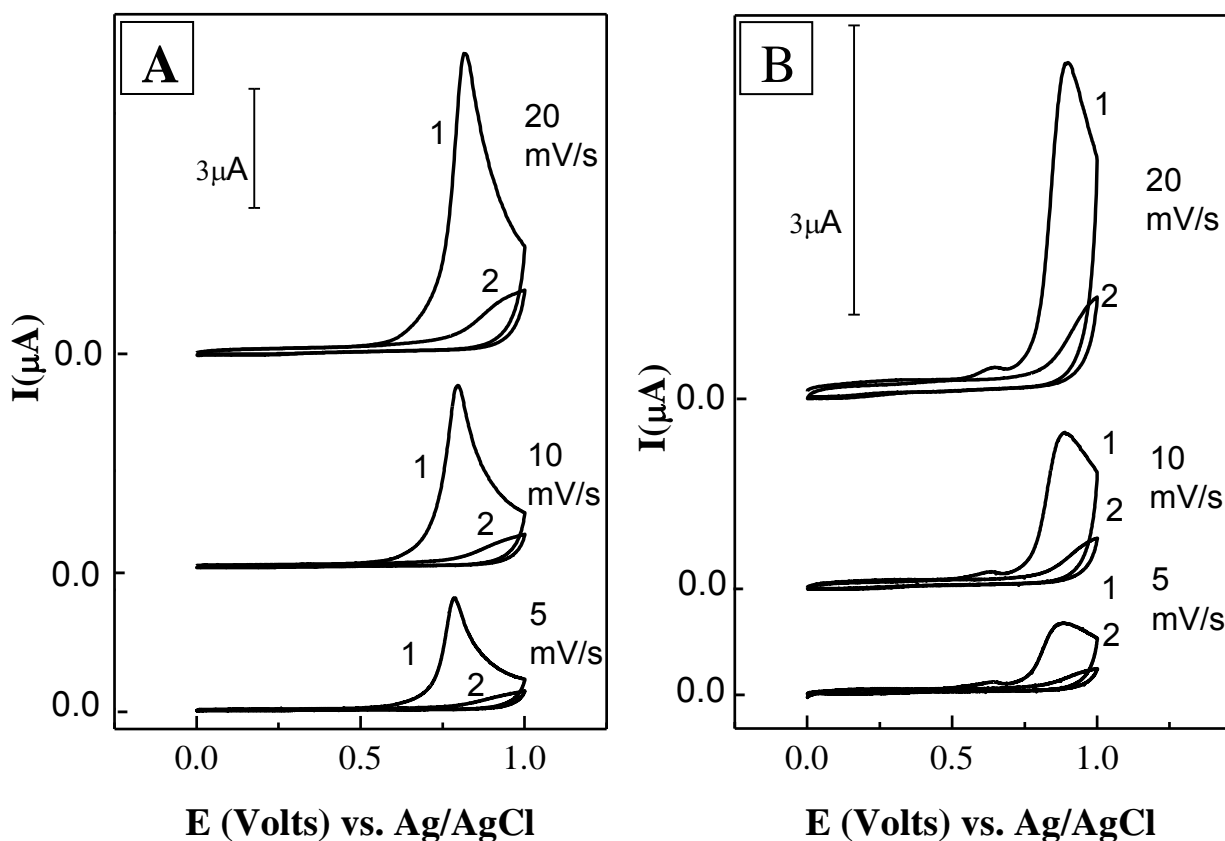
**Table 1.** HOMO and LUMO values for 1,3 dihydroxybenzene, 3-hydroxybenzyl alcohol and ionised forms of both with the corresponding geometrical plots.

		E_HOMO (eV)	HOMO Plots	E_LUMO (eV)	LUMO Plots
A		-8.57		3.43	
B		-8.42		3.8	
C		2.52		11.91	



**Figure 2.** Schematic for the electrochemical oxidation and dimerization of 3-hydroxybenzyl alcohol from neutral and acidic solutions.

The oxidation and polymerisation potentials of 1,3 dihydroxybenzene and 3-hydroxybenzyl alcohol in 0.1 M sulphuric acid (both solutions having a pH of 0.9) are shifted anodically (see Fig. 3A and 3B) indicating that it is more difficult to oxidise and polymerise both compounds in acidic solutions. Analysis of such cyclic voltammograms is not trivial as a multitude of chemical and electrochemical reactions, as described previously, occur both in sequence and in parallel. The mechanisms of oxidation and polymerisation described in the literature (adapted here to 3-hydroxybenzyl alcohol) are not explicit as to whether the loss of hydrogen occurs concomitant with (wherein the oxidation potentials would be a function of pH as described by the Nernst equation) or post oxidation of the compound. In the scenario whereby hydrogen is lost in a chemical reaction post oxidation then it is likely that such reactions are hindered in acidic solutions, due to the high concentration of hydronium ions in acidic solutions, shifting the measured potentials to higher values.

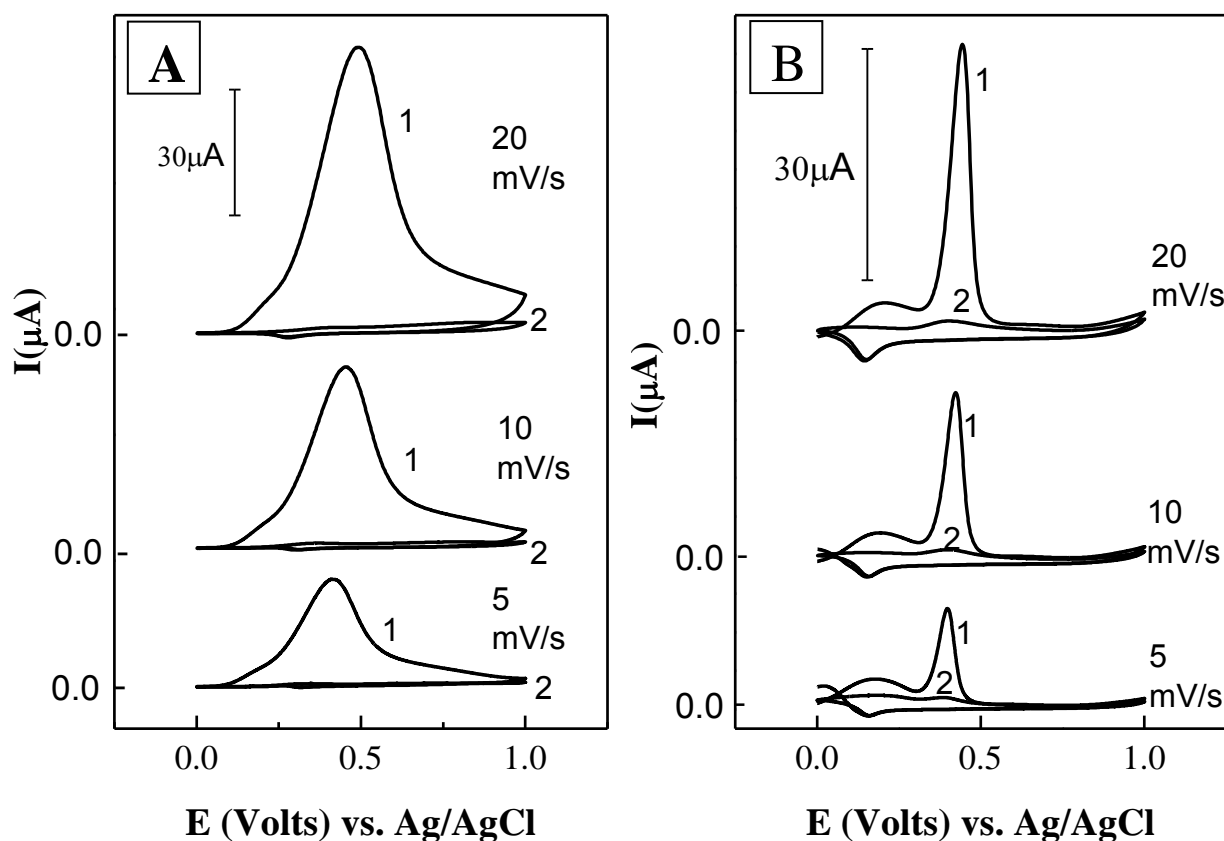


**Figure 3.** Cyclic voltammograms for the oxidation and polymerisation of solutions in 100 mM sulphuric acid of (A) 100 mM 1,3 dihydroxybenzene and (B) 100 mM 3-hydroxybenzyl alcohol .

The pKa of 3-hydroxybenzyl alcohol is 9.8 [10], the first pKa of 1,3 dihydroxybenzene is 9.2/9.4 [15, 13] and the second pKa of 1,3 dihydroxybenzene is 10.9 [15]. Consequently the species that can be oxidised in alkaline solutions are varied in comparison to neutral and acidic solutions. The energy of the HOMOs of the various ionised species of 1,3 dihydroxybenzene and 3-hydroxybenzyl alcohol are much higher (see table 1) than the unionised molecules. Therefore oxidation and

polymerisation of 3-hydroxybenzyl alcohol and 1,3 dihydroxybenzene from alkaline solutions should be easier than from neutral and acidic solutions (versus a pH insensitive reference electrode).

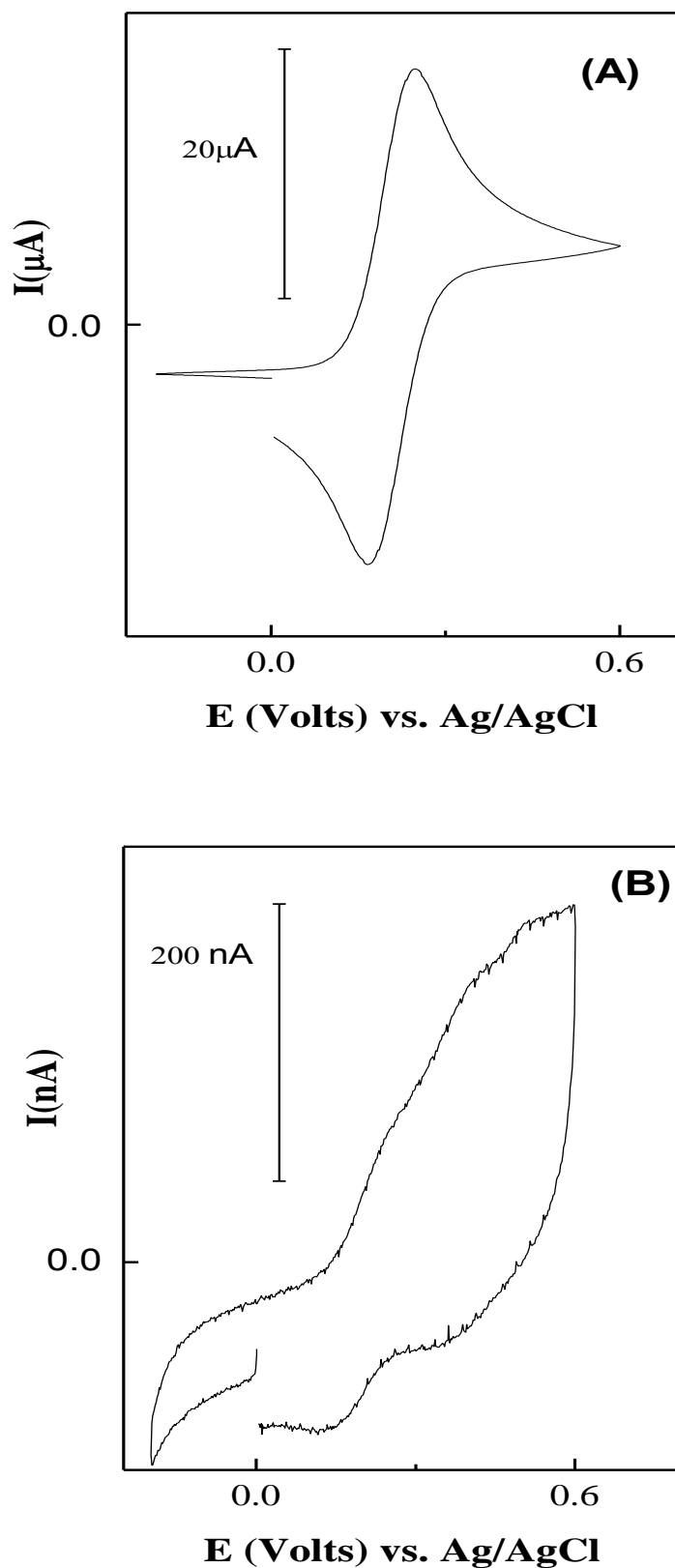
This is demonstrated in Fig. 4A and 4B where the potentials at which oxidation and polymerisation occurs in alkaline solutions are much lower than for acidic and neutral solutions. The pH of the 100 mM of 1,3 dihydroxybenzene in 100 mM sodium hydroxide is 10.5. Consequently the monovalent anion of 1,3 dihydroxybenzene will predominate in solution but a small proportion of the divalent anion may also be present. The pH of the equivalent solution of 3-hydroxybenzyl alcohol is 10.9 and the compound will exist almost exclusively in an ionised state.



**Figure 4.** Cyclic voltammograms for the oxidation and polymerisation of solutions in 100 mM sodium hydroxide of (A) 100 mM 1,3 dihydroxybenzene and (B) 100 mM 3-hydroxybenzyl alcohol.

Conclusive proof of the presence of a polymer film on the electrode surface is shown in Fig. 5. Fig. 5A presents a typical cyclic voltammogram run of a gold electrode after mechanical polishing with a slurry of 0.05 $\mu$ m Alumina powder. After the polishing stage, same electrode was immediately electrochemically tested in a 5mM ferri/ferro cyanide, 100mM KCl solution. In contrast Fig. 5B presents a typical cyclic voltammogram run of the same gold electrode tested in the same solution after electropolymerisation of 3HBA from a basic solution. It can be clearly seen that the current is dropped sharply into the nano range and the smooth peaks feature was totally disappeared from the scans.

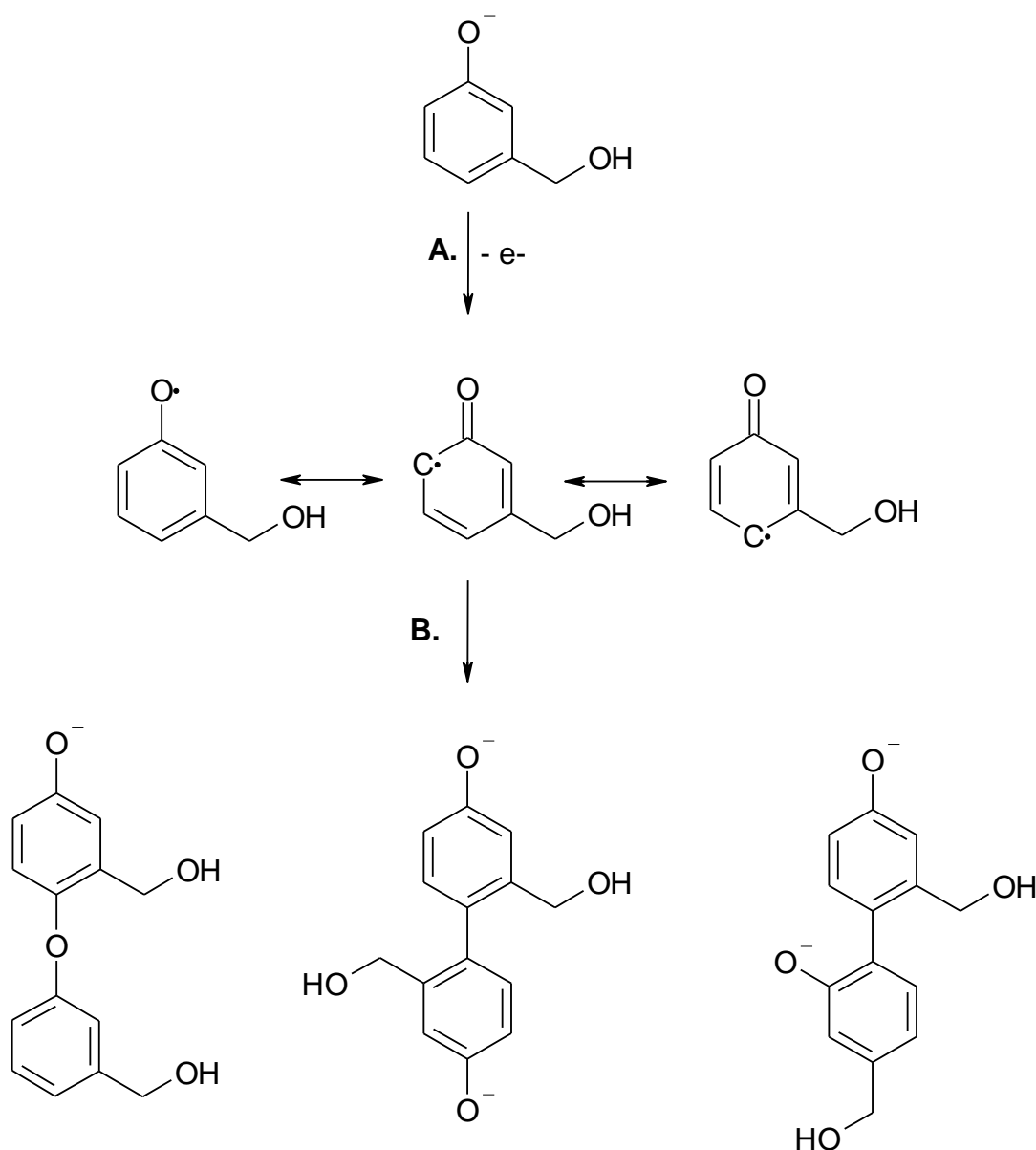




**Figure 5.** (A) A typical cyclic voltammogram run of polished gold electrode tested in 5mM ferri/ferrocyanide 100mM KCl solution (before polymerisation), (B) A typical cyclic voltammogram run of the same gold electrode after the polymerisation of 3HBA in 100mM sodium hydroxide.

The oxidation and dimerization reactions of 3-hydroxybenzyl alcohol must therefore also be different and are shown in Fig. 6. The most obvious difference is that, as the monomer is already ionised, 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.

Another notable feature of the cyclic voltammograms is that the currents in alkaline solutions are much higher than in acidic or neutral solutions. This would indicate that that either monomer oxidation can occur at a much higher rate relative to polymerisation or that the polymer formed is more conductive allowing for continuing electrochemical reactions even after polymer deposition has occurred.



**Figure 6.** Schematic for the electrochemical oxidation and dimerization of 3-hydroxybenzyl alcohol from neutral and acidic solutions.

#### 4. CONCLUSIONS

Both 1,3 dihydroxybenzene and 3-hydroxybenzyl alcohol can be electrochemically oxidised and polymerised from neutral, acidic and basic aqueous solutions. It is shown that the calculated HOMO energy values of both molecules can explain the nature of the electrode reactions at different pH values. It is further demonstrated that the pendant benzyl alcohol groups on 3-hydroxybenzyl alcohol do not participate in the electrochemical reactions. These groups are therefore available for further modification providing a chemical route for increasing specificity for the fabrication of biosensors.

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