



The Electrochemical polymerisation of 1,2 dihydroxybenzene and 2-hydroxybenzyl alcohol prepared in different solutions media



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ABSTRACT

The electrochemical polymerisation of 1,2 dihydroxybenzene (catechol) and 2-hydroxybenzyl alcohol (2HBA) from aqueous neutral, acidic and basic solutions was investigated. The development of polymer films on gold working electrodes was observed by the rapid decrease in current seen in the cyclic voltammograms (CV). The currents pertaining to the oxidation and polymerisation of catechol are far higher (by some two orders of magnitude) than for the 2HBA in all tested media. The presence of polymer films was confirmed by the decrease in current in the CV scans subsequent to the first. Molecular structures, electron density distribution and the eigenvalues of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of each compound and their ionised forms were calculated using Spartan 14 V1.1.4 molecular modelling suite package. All values have been carried out by restricted Hartree–Fock (RHF) level using 6–311G* basis set. The calculated energy levels were used to evaluate the electrochemical event.

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1. Introduction

The electrochemical polymerisation of 1,2 dihydroxybenzene has not been studied in great depth. Carelli et al. [1] studied the co-polymerisations of di-hydroxybenzenes and diamino benzenes with a view to their application in the construction of biosensors for the detection of hydrogen peroxide. In a measure of their ability to screen common interferences, it was found that co-polymers containing 1,3-dihydroxybenzene outperformed those of 1,2-dihydroxybenzene. Davis et al. [2] demonstrated that the presence of 1,2-dihydroxybenzene in solution whilst electropolymerising 1,2-phenylenediamine, resulted in a significant increase in the incorporation of phenazine redox groups into the polymer backbone.

Davis et al. [3] also studied the polymerisation of 1,2-dihydroxybenzene and various derivatives in buffered solutions

at pH 7. Khoo and Zhu [4] polymerised 1,2-dihydroxybenzene from neutral and caustic solutions at glassy carbon electrodes. They found that films of poly 1,2-dihydroxybenzene responded selectively to Ce(III) and a basic sensor was developed. Kong and Mu [5] studied the polymerisation of 1,2-dihydroxybenzene at a rotating ring disc electrode from pH 1 to 10. It is claimed that electron spin resonance of the films demonstrates that the films contain unpaired electrons. The same authors [6] studied the polymerisation of 1,2-dihydroxybenzene at platinum electrodes over acidic and basic pH ranges.

Qian et al. [7] studied the incorporation of platinum particles into electropolymerised 1,2-dihydroxybenzene films. SEM images showed that platinum particles could be evenly distributed into the polymer film. The catalytic activity of this composite film for the oxidation of methanol was significantly greater than for electrodeposited films of platinum. Marczevska and Przegalinski [8] studied the polymerisation of 1,2-dihydroxybenzene at glassy carbon electrodes.

Pham et al. [9] investigated the oxidation and polymerisation of 2-hydroxybenzyl alcohol in a basic methanol solution and obtained thin polymer films. 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

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oxidation potentials, pKa and the energy of the highest occupied molecular orbital (HOMO) of the molecules in different states of ionisation.

2. Experimental

2.1. Chemicals

All chemicals were analytical grade and used without further purification. 2-hydroxybenzyl alcohol (2HBA) (98%), 1,2 dihydroxybenzene (99%), potassium chloride (99%), potassium ferrocyanide trihydrate (>98%), potassium ferricyanide (>98%) were all procured from Alfa Aesar, Germany. Sodium hydroxide (98%) and Sulphuric acid (95–98%) were purchased from PRS, Panreac, Spain.

2.2. 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 μm 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^{-1} for 2 sweeps of potential.

2HBA and 1,2 dihydroxybenzene were then oxidatively electro-polymerised onto 1.6 mm diameter gold electrodes. Concentrations of 100 mM 2HBA or 1,2 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^{-1}) 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 at the same settings as mentioned above.

2.3. 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 [10]. 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 used in the present study.

3. Results and Discussion

There are two pKa values, 9.2 and 11.7, associated with 1,2 dihydroxybenzene [8]. At the first pKa of 9.2 the neutral molecule and monovalent anion co-exist at equal concentration. The monovalent and divalent anions have equal concentrations at

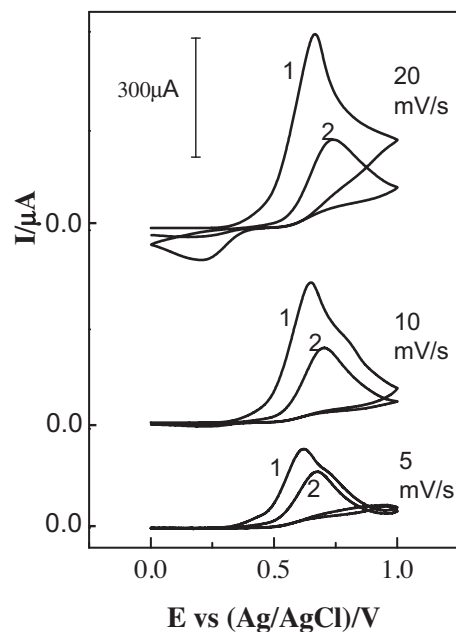


Fig. 1. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 1,2 dihydroxybenzene in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

the second pKa of 11.7. Consequently the species that may be electrochemically oxidised is dependent on the pH of the solution.

In contrast 2-hydroxybenzyl alcohol has only one pKa value of 9.92 [11] related to the ionisation of the hydroxyl group on the benzene ring. The hydroxyl group not bonded directly to the benzene ring behaves similarly to benzyl alcohol, an aromatic compound with a pKa in excess of 15. The phenoxide ion, produced by the ionisation of phenol, is stabilised by the resonance interaction of the negative charge with the carbon atoms on the

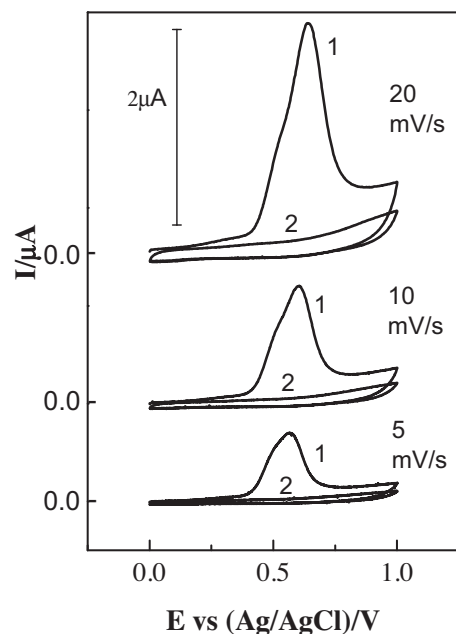
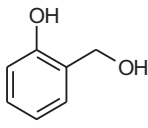

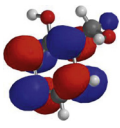
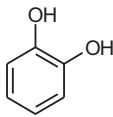
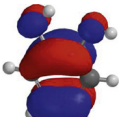
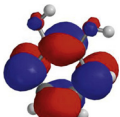
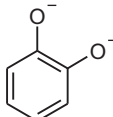

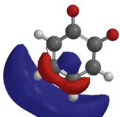
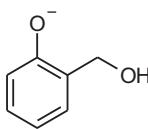
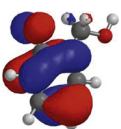
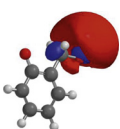
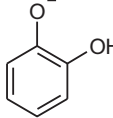
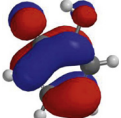



Fig. 2. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 2-hydroxybenzyl alcohol in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

Table 1

Molecular structure, eigenvalues for HOMO and LUMO molecular orbitals and electron density distribution for 2-hydroxybenzyl alcohol, 1,2-dihydroxybenzene, and their ionised forms. All values were calculated using Spartan 14 V1.1.4 molecular modelling suite package.

| | | E_HOMO (eV) | HOMO Plots | E_LUMO (eV) | LUMO Plots |
|---|--|-------------|--|-------------|--|
| A |  | -8.5 |  | 3.6 |  |
| B |  | -8.3 |  | 3.8 |  |
| C |  | 3.7 |  | 11.8 |  |
| D |  | -2.0 |  | 7.5 |  |
| E |  | -2.1 |  | 8.1 |  |

benzene ring. This stabilisation is not possible for the anion of benzyl alcohol and thus it has a pKa similar to that of simple aliphatic alcohols.

It is postulated [12] in electrochemical theory that redox reactions of chemical species in solution are governed by the energy of the HOMO relative to the energy of the electrons in the Fermi level of the electrode. Species with HOMOs of lower energy are oxidised at potentials more anodic than species of higher HOMO energy. In Figs. 1 and 2 cyclic voltammograms for the oxidation and polymerisation of 1,2 dihydroxybenzene and 2-hydroxybenzyl alcohol in neutral solutions are presented. The onset and peak potentials for oxidation and polymerisation are comparable for both compounds. The energies of the HOMOs of the uncharged molecules (predominant at neutral pH), shown in Table 1, are very similar explaining the observed electrochemical behaviour.

The currents pertaining to the oxidation and polymerisation of 1,2 dihydroxybenzene are far higher (by some two orders of magnitude) than for the 2-hydroxybenzyl alcohol. Oxidation and polymerisation reactions will only initially occur at the metal solution interface and will thereafter occur at a polymer solution interface indicating that a thicker polymer film is probably formed from the oxidation of 1,2 dihydroxybenzene than from the oxidation of poly 2-hydroxybenzyl alcohol. The presence of polymer films is confirmed by the decrease in current in scans subsequent to the first.

The mechanism for the electrochemical oxidation, dimerization and subsequent polymerisation of phenol has been established by

Gattrell and Kirk [13]. 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. That this reaction also occurs for 1,2 dihydroxybenzene is supported by Marczevska and Przegalinski [8] who determined that the initial oxidation of 1,2 dihydroxybenzene involves the transfer of one electron only.

Dimerisation of monomers with phenol functionality occurs more through carbon-carbon coupling of aromatic rings than through carbon-oxygen coupling provided that such coupling is not sterically hindered [13]. Such carbon-carbon linked dimers are free to polymerise through the hydroxyl group leading to a highly cross-linked insoluble polymer with monomer concentration, electrode material, reactant adsorption characteristics, pH, current density and voltage all being important in determining what reaction pathway is followed. The monomer 2-hydroxybenzyl alcohol will oxidise and dimerise in a similar fashion to phenol and the reactions are outlined in Fig. 3. 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.

For 1,2 dihydroxybenzene the potentials at which oxidation starts and peak currents are observed appears to shift by ~100 mV in 0.1 M sulphuric acid (the solution pH being 0.7) from what they are in neutral solutions, see Fig. 4. The compound is, for the most part, not ionised in acid and neutral solutions demonstrating that

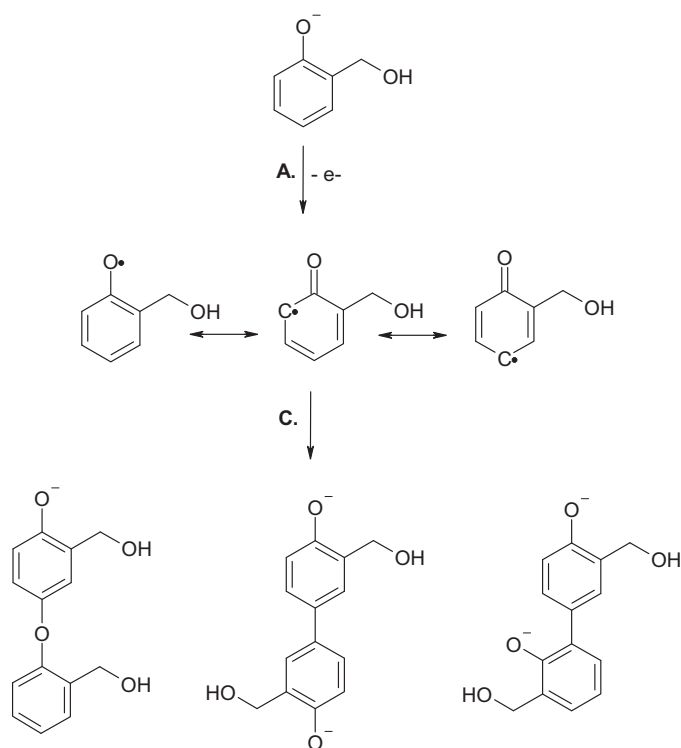


Fig. 3. Oxidation and dimerization of 2-hydroxybenzyl alcohol in neutral and acidic solutions.

the oxidation and polymerisation reactions are not pH dependent, in acidic solutions. There are secondary peaks at 0.75 V, for a sweep rate of 5 mV/s and 0.8 V, for a sweep rate of 10 mV/s. However it is difficult, and perhaps imprudent, to speculate on the nature of these peaks given the difficulty in identifying the multitude of compounds can be formed upon initial oxidation of 1,2 dihydroxybenzene.

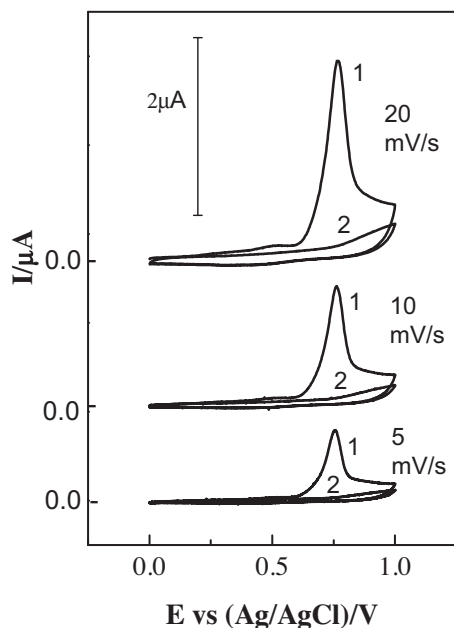


Fig. 5. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 2-hydroxybenzyl alcohol in 100 mM sulphuric acid using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

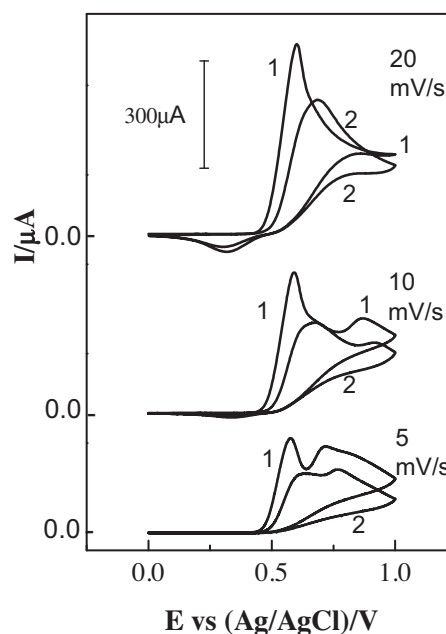


Fig. 4. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 1,2 dihydroxybenzene in 100 mM sulphuric acid using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

In contrast the same potentials for 2-hydroxybenzyl alcohol in 0.1 M sulphuric acid (the solution pH being 0.6) are shifted anodically (see Fig. 5) by some 200 mV indicating that it is more difficult to oxidise and polymerise the compound in acidic solutions. The analysis of such cyclic voltammograms is not straightforward as a multitude of chemical and electrochemical reactions can occur both concurrently and consecutively. The mechanisms of oxidation and polymerisation as published in the literature (and adapted in Fig. 3) are not clear as to whether the loss of hydrogen occurs simultaneously with (wherein the oxidation potentials would be a function of pH as described by the Nernst equation) or post oxidation of the compound.

An anodic shift in potential of this order (~ 30 mV for each unit of pH) indicates that the electrochemical reaction might involve two protons. An alternative explanation is that the high concentration of hydronium ions in acidic solutions impedes the dimerization and polymerisation reactions as such reactions require the loss of protons from the oxidised molecules. That this shift in potentials is not seen for 1,2 dihydroxybenzene points to certain differences in the electrochemical oxidation of the compounds also illustrated by the much higher currents observed for the oxidation of and polymerisation of 1,2 dihydroxybenzene.

The pH of the basic solutions from which 1,2 dihydroxybenzene was polymerised was 11.7 and at this pH (the pKa of 1,2 dihydroxybenzene) the monovalent and divalent ion co-exist at equal concentrations. This perhaps explains the complicated nature of the cyclic voltammograms on the first and subsequent scans, shown in Fig. 6. It is also clear that the oxidation of the monomer starts at much lower potentials than in acidic and neutral solutions. This is explained by the increased energy of the HOMO of both the monovalent and divalent ions as shown in Table 1. There are multiple indistinct peaks in each scan and it is difficult to determine the exact nature of each peak given the difficulty in identifying the multitude of compounds can be formed upon initial oxidation of 1,2 dihydroxybenzene.

The pH of the basic solutions from which 2-hydroxybenzyl alcohol was polymerised was 11.9 and at this pH 2-hydroxybenzyl

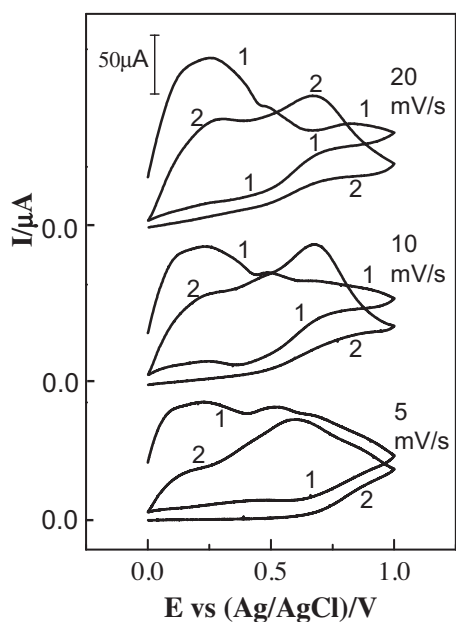


Fig. 6. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 1,2-dihydroxybenzene in 100 mM sodium hydroxide using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

alcohol exists in an ionised form. The energy of the HOMO of the ionised form of 2-hydroxybenzyl alcohol is very similar to that of the monovalent ion of 1,2-dihydroxybenzene. Therefore oxidation and polymerisation of 2-hydroxybenzyl alcohol from alkaline solutions should be easier than from neutral and acidic solutions (versus a pH insensitive reference electrode) as is seen for 1,2-dihydroxybenzene.

This is demonstrated in Fig. 7 where the potentials at which oxidation and polymerisation occurs in alkaline solutions are much lower than for acidic and neutral solutions. The shape of the cyclic voltammograms is quite different to those of 1,2-dihydroxybenzene and the currents are much lower, illustrating once more the different nature of the polymerisation reactions.

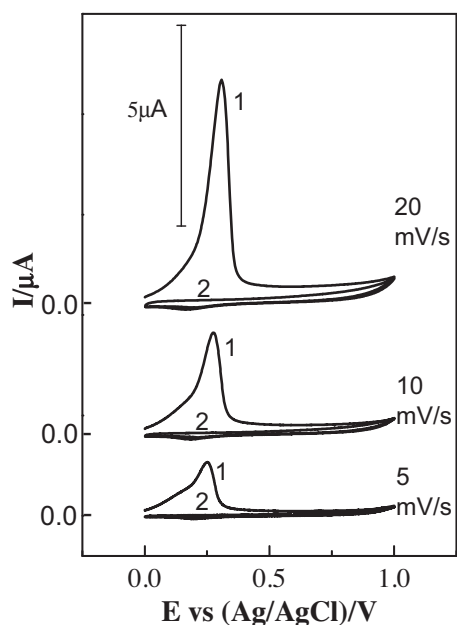


Fig. 7. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 2-hydroxybenzyl alcohol in 100 mM sodium hydroxide using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

Conclusive proof of the presence of a polymer film on the electrode surface is shown in Fig. 8. Fig. 8A presents a typical cyclic voltammogram run of a gold electrode after mechanical polishing with a slurry of 0.05 μm alumina powder. After the polishing stage, same electrode was immediately electrochemically tested in a 5 mM ferri/ferro cyanide, 100 mM KCl solution. In contrast Fig. 8B presents a typical cyclic voltammogram run of the same gold electrode tested in the same solution after electropolymerisation of 2HBA 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 2-hydroxybenzyl alcohol in alkaline solutions must also be different and are shown

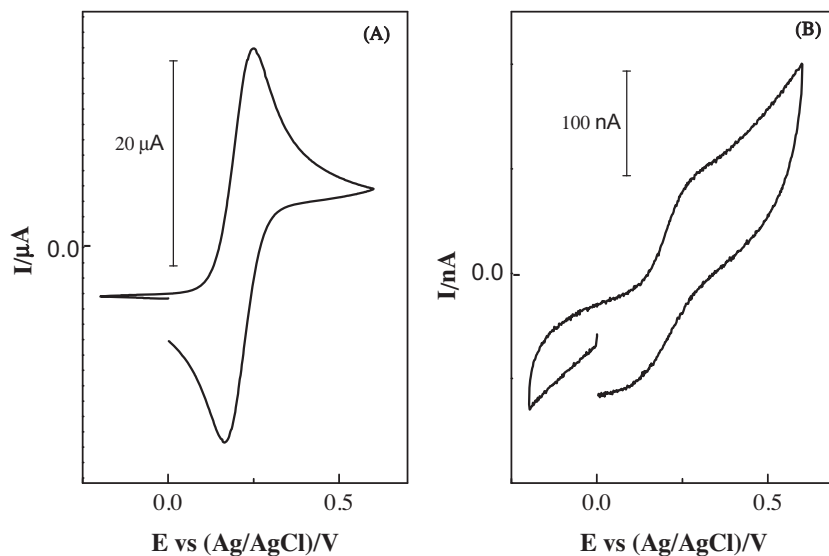


Fig. 8. (A) A typical cyclic voltammogram run of polished gold electrode tested in 5 mM ferri/ferro cyanide 100 mM KCl solution (before polymerisation), (B) A typical cyclic voltammogram run of the same gold electrode after the polymerisation of 2HBA in 100 mM sodium hydroxide.

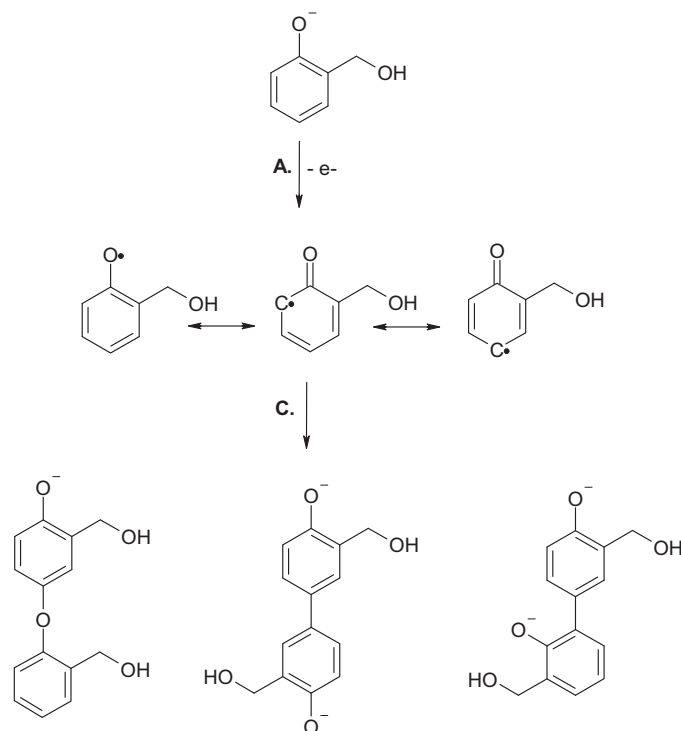


Fig. 9. Oxidation and dimerization of 2-hydroxybenzyl alcohol in basic solutions.

in Fig. 9. 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.

4. Conclusions

The compounds 1,2 dihydroxybenzene and 2-hydroxybenzyl alcohol can both be electrochemically oxidised and polymerised from neutral, acidic and basic aqueous solutions. In general the currents associated with the oxidation of 1,2-dihydroxybenzene are much higher than those associated with 2 hydroxybenzyl alcohol. The oxidation potentials of 1,2-dihydroxybenzene are in general lower than those associated with 2 hydroxybenzyl alcohol. Chemically this can in part be explained by the resonance interaction permitted for the hydroxyl groups of 1,2-dihydroxybenzene and the absence of such interaction for 2-hydroxybenzyl alcohol. Furthermore the calculated HOMO energy values of the molecules explain the contrasting nature of the electrode reactions at different pH values.

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