



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 diaminobenzenes 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

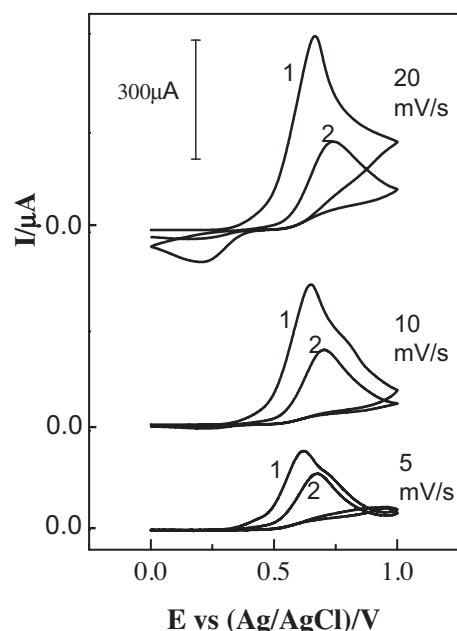


Fig. 1. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 1,2 dihydroxybenzene in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

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

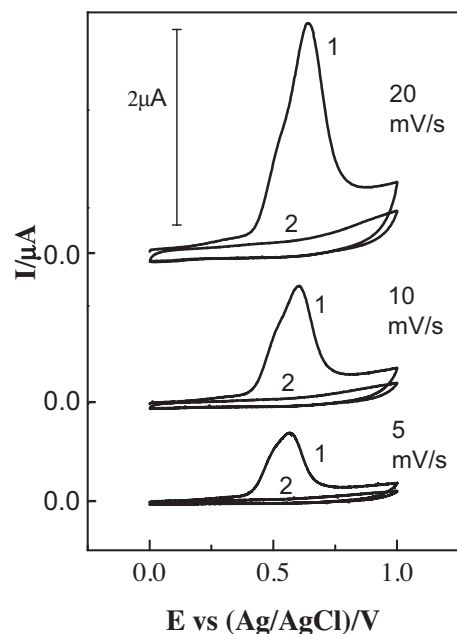


Fig. 2. Cyclic voltammograms for the oxidation and polymerisation of 100 mM 2-hydroxybenzyl alcohol in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

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