

Electrochemical studies of 3-aminophenol and 3-aminobenzyl Alcohol in Aqueous Solutions at Different pH Values

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The electrochemical oxidation and polymerisation of 3-aminophenol and 3-aminobenzyl alcohol in aqueous solutions of different pH values has been studied. The deposition of polymer films on gold electrodes from solutions of the studied monomers were demonstrated by the rapid decrease in current observed in cyclic voltammograms (CVs) subsequent to the first scan. In general the oxidation potentials for 3-aminobenzyl alcohol are higher than for 3-aminophenol for solutions of similar pH.

Keywords: oxidation; electropolymerisation; thin film; voltammetry

1. INTRODUCTION

The electrochemical polymerisation of aniline has been studied by many authors [1, 2] but no work has been published on the electropolymerisation of 3-aminobenzyl alcohol. Few researchers have worked on the electrochemical polymerisation of 3-aminophenol. It has been studied by Prater[3] in the medium of acetonitrile generating insulting polymer films on the electrode surface.

Barbero et al [4] studied 2-aminophenol and Taj et al [5] similarly studied 2-aminophenol and 3-aminophenol respectively with similar results to those of Prater. Sankarapavinasam [6, 7] has also studied the electrochemical polymerisation of 3-aminophenol determining that polymerisation rate was dependent on concentration at low current densities. Nakabayashi [8, 9] used poly (3-aminophenol) films in their study of biosensors as have Fung et al.[10] in their work on biosensors for the detection of *Salmonella Enteritidis*.

In this paper the electrochemical behaviour of 3-aminophenol will be compared with that of 3-aminobenzyl alcohol in aqueous solutions of different pH values. The synthesized polymer films can be

used for applications such as corrosion protection, and as structures from which textured electrodes, microelectrode arrays for example, can be generated.

2. EXPERIMENTAL

2.1 Chemicals

All chemicals were analytical grade and used without further purification. 3-aminophenol (>98%), 3-aminobenzyl alcohol (>98%), 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) 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 deionised water for a few minutes, in order to remove any residual alumina. The polished electrode was then electrochemically tested using a solution of 5.0 mmol L⁻¹ ferri/ferro cyanide containing 0.1 mol 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.

3-aminophenol and 3-aminobenzyl alcohol were electrochemically polymerised at 1.6 mm diameter gold electrodes. Acidic, basic and neutral solutions of 0.1 mol L⁻¹ 3-aminophenol and 0.1 mol L⁻¹ 3-aminobenzyl alcohol were prepared using either potassium chloride (0.1 mol L⁻¹), sulphuric acid (0.1 mol L⁻¹) or sodium hydroxide (0.1 mol 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 mV 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 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 and this was done at the same settings as mentioned previously.

3. RESULTS AND DISCUSSION

There are two measured pKa values, 4.37 and 9.82, associated with 3-aminophenol[11] indicating that 3-aminophenol is amphoteric and will exist primarily as the neutral species at pH values of 5 to 9. The species to be oxidised depends on the pH of the solution in solutions with acid concentration below the first pKa of 4.37 the monovalent cation (formed by the protonation of the

amino group) predominates and the monovalent anion (formed by the deprotonation of the hydroxyl group) predominates above the second pKa of 9.82. An exhaustive search of the literature shows that the pKa of 3-aminobenzyl alcohol has not been published but it is likely to have a pKa value close to that of 2-aminobenzyl alcohol, which is 3.5[12] related to the ionisation of the amino group on the benzene ring. The hydroxyl group which is not bonded directly to the benzene ring behaves similarly to benzyl alcohol, an aromatic compound with a pKa in excess of 15.

The oxidation and polymerisation of 3-aminophenol and 3-aminobenzyl alcohol in neutral solutions, at which pH the uncharged species predominate, was studied by cyclic voltammetry and results are presented in Fig. 1A and B. The onset and peak potentials for oxidation and polymerisation are different for both compounds, being 0.25 and 0.45 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl for 3-aminophenol and 0.4 and 0.6 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl for 3-aminobenzyl alcohol. For both compounds scans subsequent to the first exhibit much lower currents demonstrating that an insulating polymer film is formed by the electropolymerisation reactions.

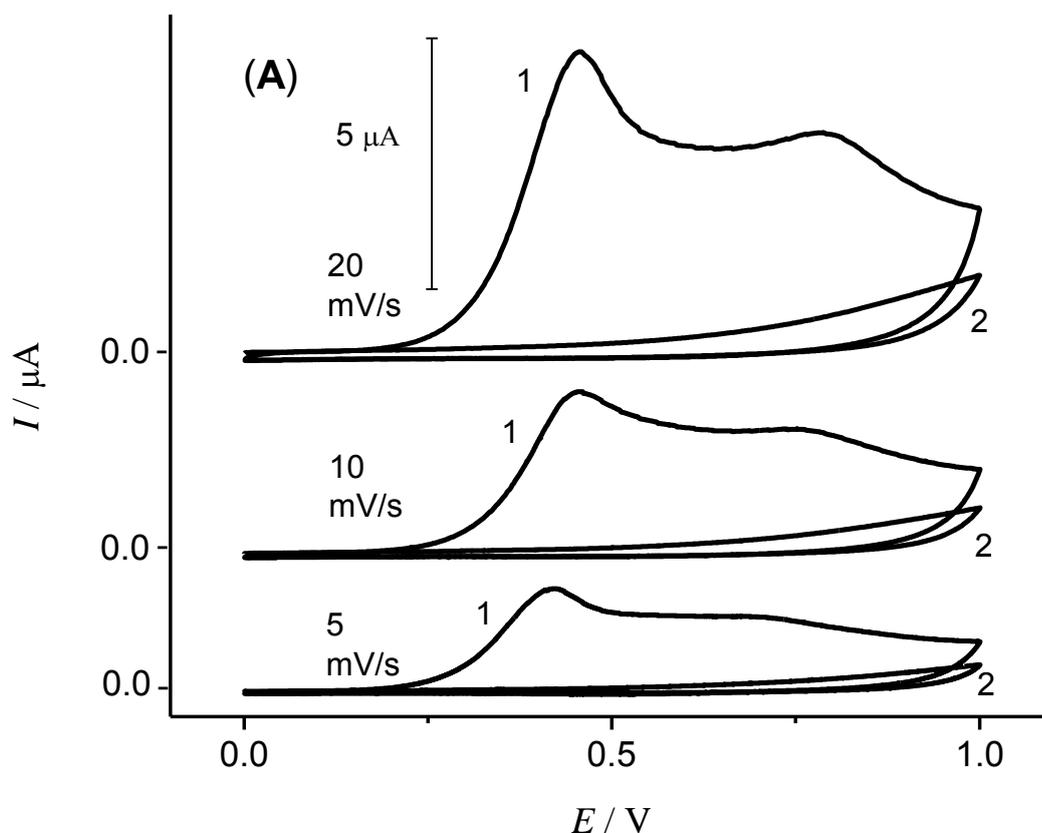


Figure 1A. Cyclic voltammograms for the oxidation and polymerisation in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates of 0.1 mol L⁻¹ of 3-aminophenol. The first two CV's shown at each sweep rate.

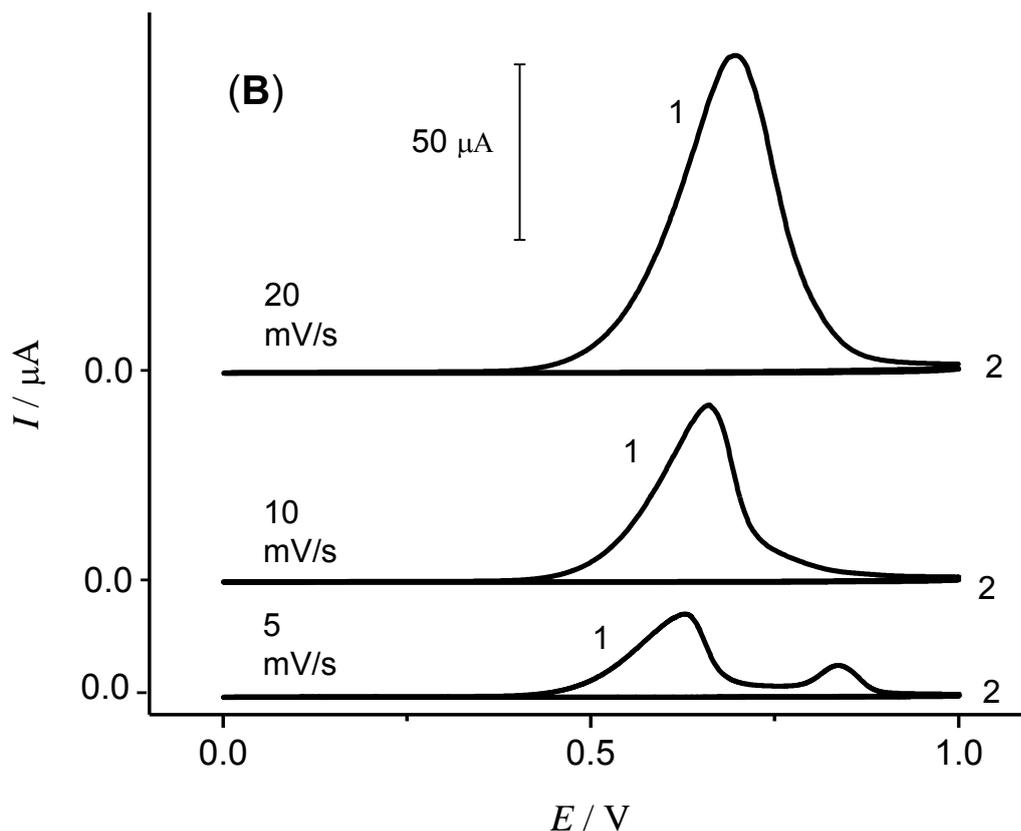


Figure 1B. Cyclic voltammograms for the oxidation and polymerisation in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates of 0.1 mol L^{-1} of 3-aminobenzyl alcohol. The first two CV's shown at each sweep rate.

The oxidation of 3-aminophenol at neutral pH first proceeds by the loss of an electron from the lone pair on the nitrogen atom as shown by Kennedy et al.[13] The oxidation of 3-aminobenzyl alcohol, as shown in Fig. 2A, occurs in a similar fashion as the aliphatic alcohol group does not participate in electrochemical oxidation reactions. The radical cation formed upon the oxidation of 3-aminophenol is not stabilized by resonance structures as the electron density cannot be relocated onto the oxygen atom, as presented in Fig. 2B. Therefore, on this basis, it could be expected that the oxidation potentials for both species should be quite similar yet a difference in potentials is seen. The oxidation of the oxygen group is not responsible for the difference as it has been demonstrated[13] that the onset potential for the oxidation of 1,3-dihydroxybenzene is 0.6 V vs. Ag/AgCl, 3.0 mol L^{-1} KCl in neutral solutions and a cause for the observed difference in potentials has as yet not been determined.

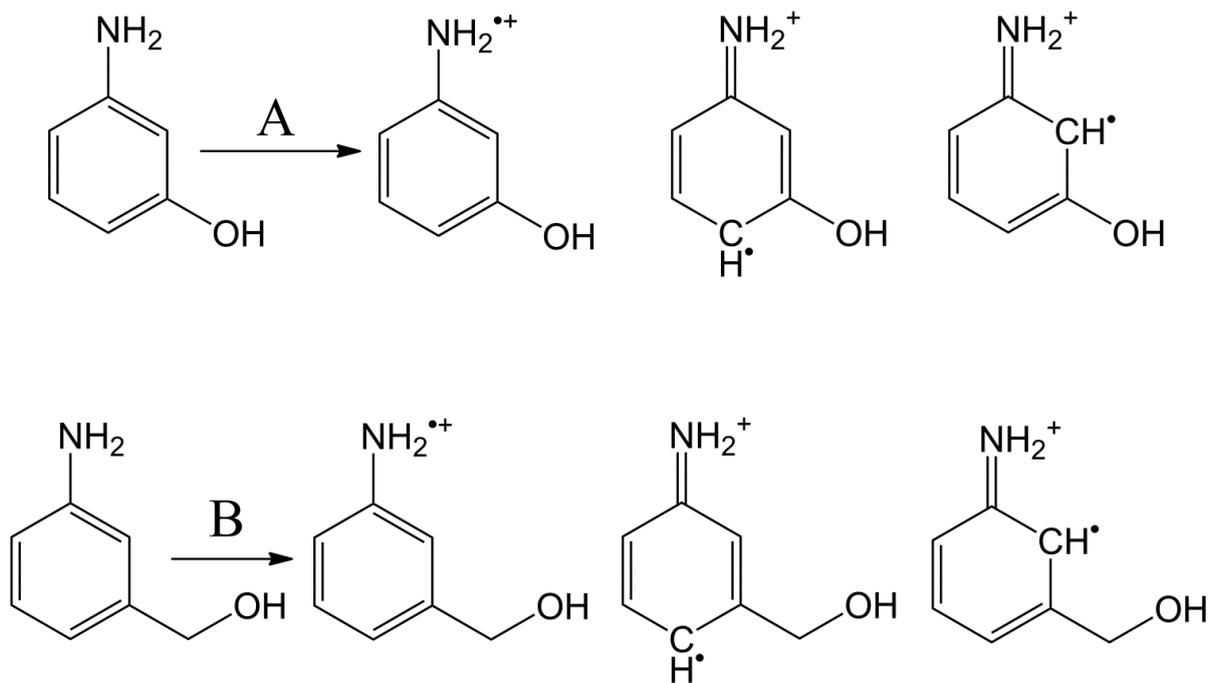


Figure 2. Oxidation of (A) 3-aminophenol and (B) 3-aminobenzyl alcohol at neutral pH.

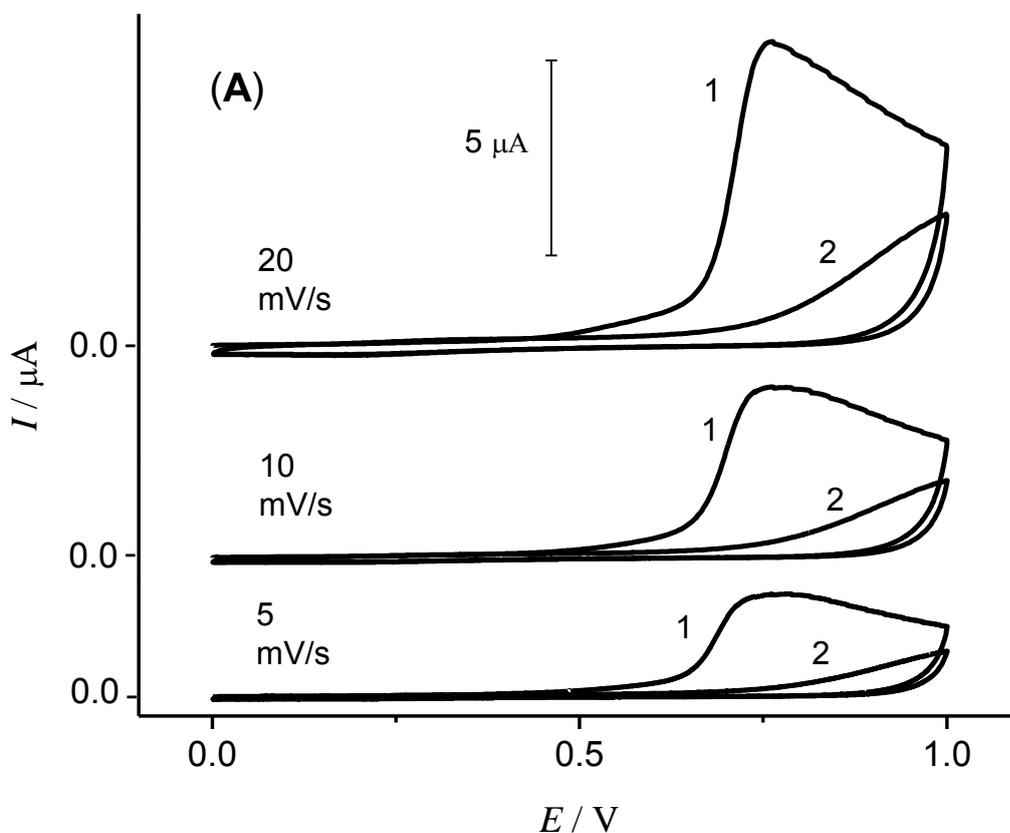


Figure 3A. Cyclic voltammograms for the oxidation and polymerisation of using a gold working electrode with a diameter of 1.6 mm at various sweep rates of 0.1 mol L^{-1} 3-aminophenol in 0.1 mol L^{-1} sulphuric acid. The first two CV's shown at each sweep rate.

The pH of solutions of both 3-aminophenol and 3-aminobenzyl alcohol in 0.1 mol L^{-1} sulphuric acid is 1.6. This is lower than the pKa value of 3-aminophenol and, with reference to the pKa of 2-aminobenzyl alcohol, is likely to be lower than the pKa of 3-aminobenzyl alcohol. It follows that the amine group of both 3-aminophenol and 3-hydroxybenzyl alcohol is protonated in these solutions. There is a significant influence on the potentials for the oxidation and polymerization of the monomers.

The onset and peak potentials are 0.5 and 0.75 V vs. Ag/AgCl, 3.0 mol L^{-1} KCl for the oxidation of 3-aminophenol (Fig. 3A) and 0.75 V and 0.9 V vs. Ag/AgCl, 3.0 mol L^{-1} KCl for 3-aminobenzyl alcohol (Fig. 3B). The potentials for 3-aminophenol are very similar to those observed for 1,3-dihydroxybenzene in 0.1 mol L^{-1} sulphuric acid as determined by Kennedy et al.[13]

This suggests that oxidation, dimerisation and polymerization of 3-aminophenol occurs through the hydroxyl group given that no lone pair of electrons are present on the nitrogen atom. The oxidation of 3-aminobenzyl alcohol is also more difficult than at neutral pH, more difficult even than for 3-hydroxybenzyl alcohol in acid solutions for which the onset and peak potentials are 0.6 V and 0.75 V vs. Ag/AgCl as determined by Barham et al.[14] This illustrates the difficulty of oxidizing aromatic species when there are no atoms bound to the benzene ring with unbonded electron pairs.

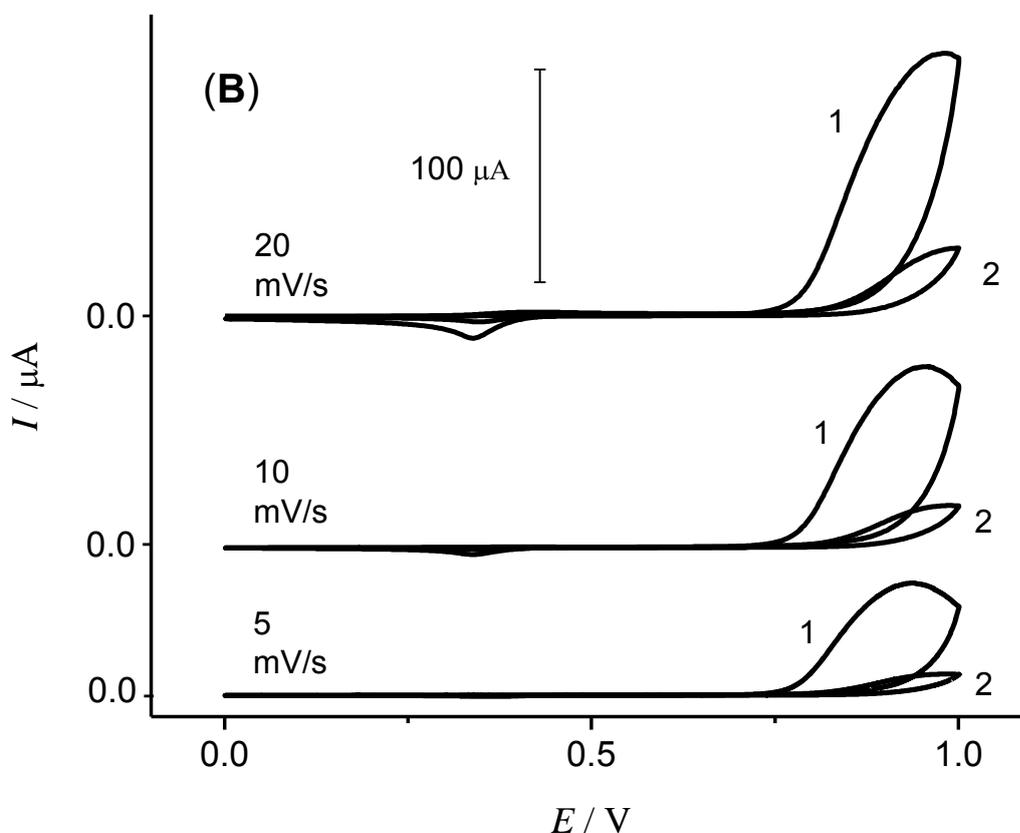


Figure 3B. Cyclic voltammograms for the oxidation and polymerisation of using a gold working electrode with a diameter of 1.6 mm at various sweep rates of 0.1 mol L^{-1} 3-aminobenzyl alcohol in 0.1 mol L^{-1} sulphuric acid. The first two CV's shown at each sweep rate.

The pH of solutions of 3-aminophenol and 3-aminobenzyl alcohol in 0.1 mol L^{-1} sodium hydroxide are 10.8 and 12.8 respectively. At this pH 3-aminophenol is a monovalent anion, a proton having been lost from the hydroxyl group, and 3-aminobenzyl alcohol is uncharged. The onset and peak oxidation potentials for 3-aminophenol (Fig. 4A) are 0 V and 0.25 V vs Ag/AgCl, 3.0 mol L^{-1} KCl. As described previously the oxidation of 3-aminophenol occurs initially at least through the loss of an electron from the lone pair of electrons on the nitrogen atom and subsequent to this reaction dimerization reaction occur that involve the elimination of protons. A possible explanation for the lower oxidation potentials is that the basic pH of the solution facilitates these reactions as the protons would be consumed in acid-base reactions as they are produced.

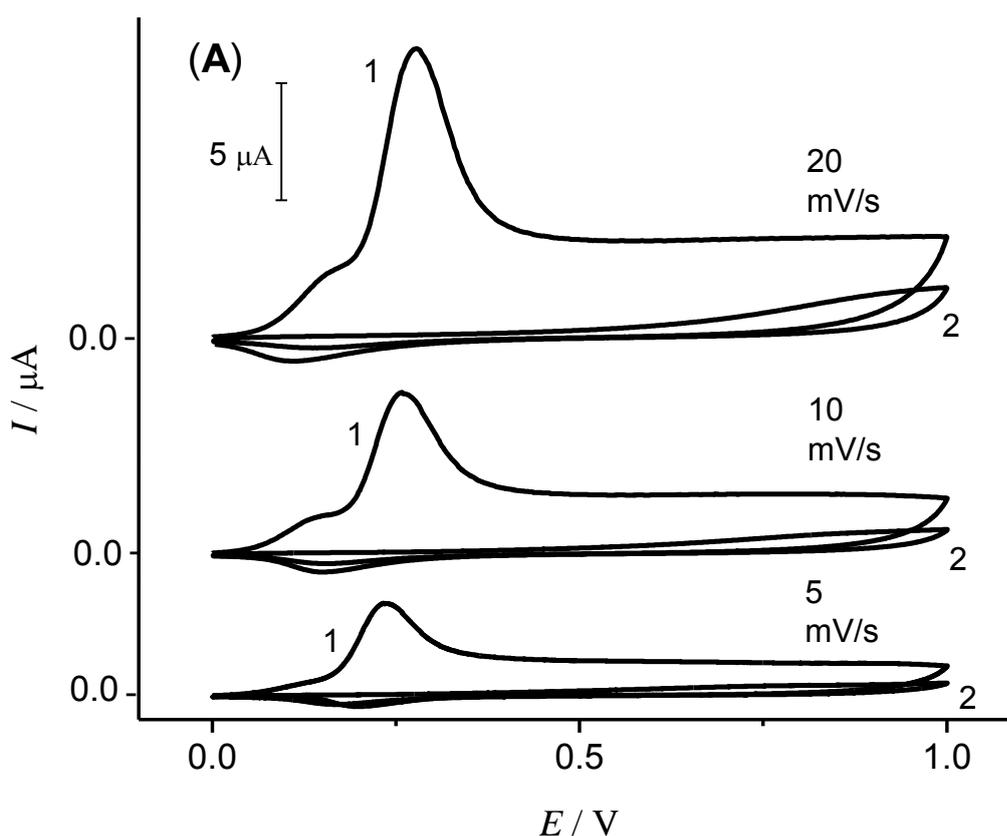


Figure 4A. Cyclic voltammograms for the oxidation and polymerisation of using a gold working electrode with a diameter of 1.6 mm at various sweep rates of 0.1 mol L^{-1} 3-aminophenol in 0.1 mol L^{-1} sodium hydroxide. The first two CV's shown at each sweep rate.

Cyclic voltammograms for the oxidation and subsequent polymerisation of 3-aminobenzyl alcohol in 0.1 mol L^{-1} sodium hydroxide are presented in Fig. 4B. The onset potential is about 0 V vs. Ag/AgCl, 3.0 mol L^{-1} KCl however the current has not risen significantly until the just before the peak potential at 0.5 V vs. Ag/AgCl, 3.0 mol L^{-1} KCl. The peak potential is very similar to the potential

observed in neutral solutions. The peak centred on 0.5 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl is highly symmetric which is suggestive of a surface confined reaction of adsorbed species at this point. The observed behaviour is quite different to that of 3-aminophenol and it is possible that oxidation of the deprotonated oxygen atom on 3-aminophenol contributes to the currents observed for this monomer explaining in part perhaps the discrepancy between the two species.

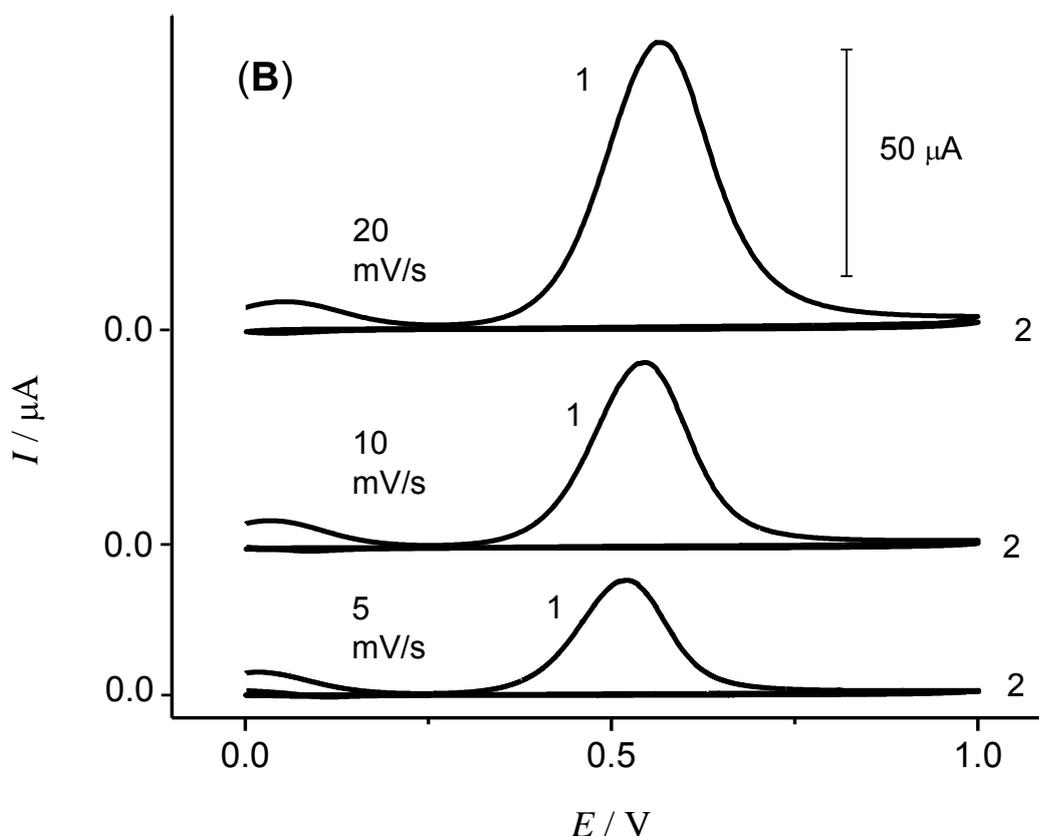


Figure 4B. Cyclic voltammograms for the oxidation and polymerisation of using a gold working electrode with a diameter of 1.6 mm at various sweep rates of 0.1 mol L⁻¹ 3-aminobenzyl alcohol in 0.1 mol L⁻¹ sodium hydroxide. The first two CV's shown at each sweep rate.

Conclusive proof of the presence of a polymer film on the electrode surface is shown in Fig. 5. A typical cyclic voltammogram run of a gold electrode after mechanical polishing with slurry of 0.05 μm alumina powder is presented in Fig. 5A. After the polishing stage the electrode was immediately tested in a 5.0 mmol L⁻¹ ferri/ferro cyanide solution containing 0.1 mol L⁻¹ KCl supporting electrolyte. In contrast, Fig. 5B presents a typical cyclic voltammogram run of the same gold electrode tested in the same solution after electropolymerisation of 3-aminobenzyl alcohol in 0.1 mol L⁻¹ sodium hydroxide. 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.

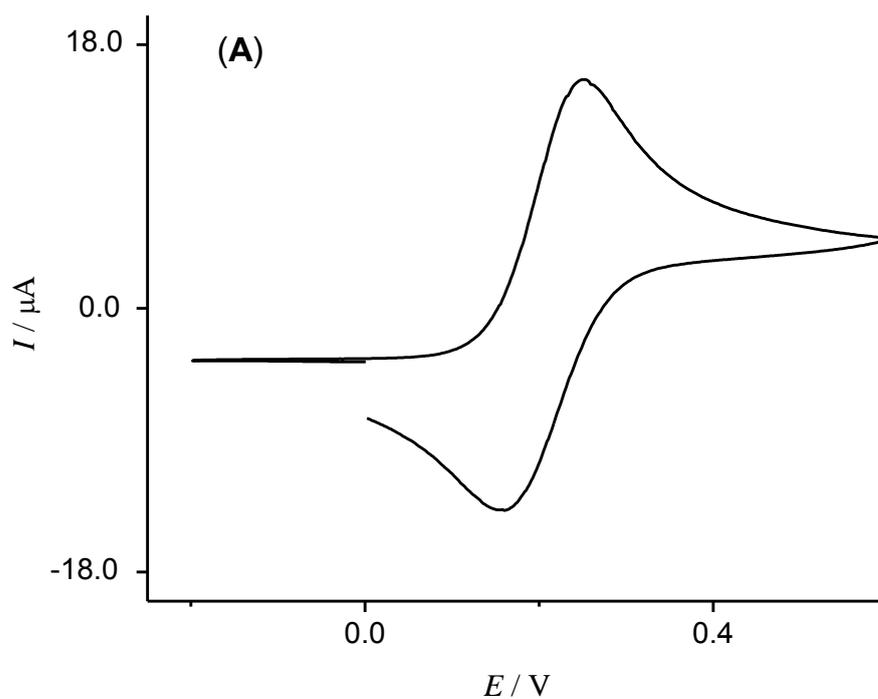


Figure 5A. A typical cyclic voltammogram run of polished gold electrode tested in 5.0 mmol L⁻¹ ferri/ferro cyanide 0.1 mol L⁻¹ KCl solution (before polymerisation).

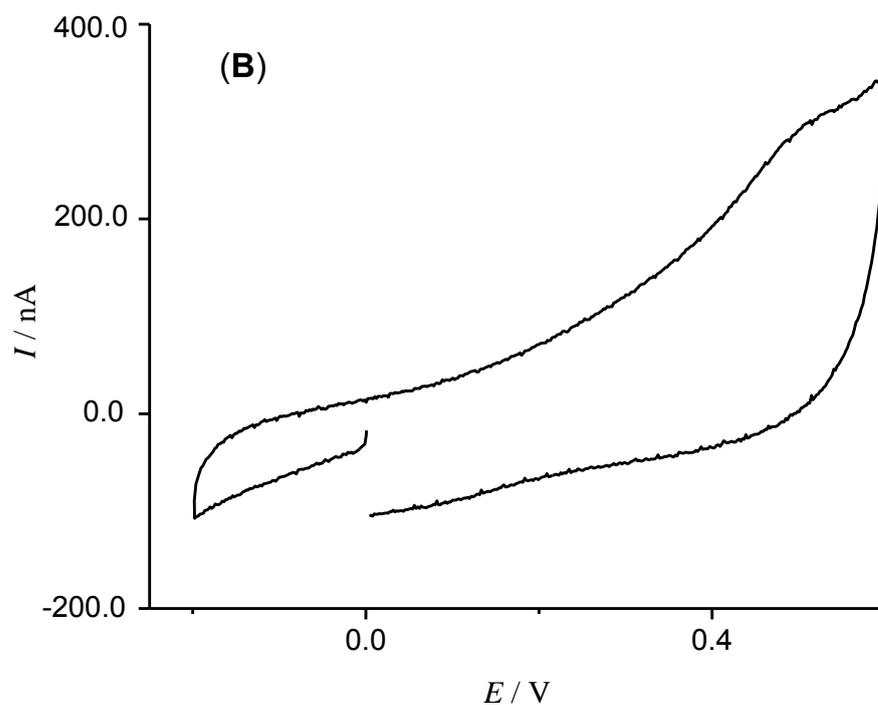


Figure 5B. A typical cyclic voltammogram run of the same gold electrode after the polymerisation of 3-aminobenzyl alcohol in 0.1 mol L⁻¹ sodium hydroxide.

4. CONCLUSIONS

The present work demonstrates that both compounds of 3-aminophenol and 3-aminobenzyl alcohol can be electrochemically oxidised and polymerised from neutral, acidic and basic aqueous solutions. As confirmed by the cyclic voltammetric experiments, oxidation and polymerisation of this 3-aminophenol and 3-aminobenzyl alcohol becomes progressively more difficult as pH decreases from basic to acidic conditions. In general the oxidation and polymerisation of 3-aminophenol occurs at lower potentials than 3-aminobenzyl alcohol. Applications for these polymer films, including corrosion protection and formation of microelectrode arrays will be considered for the future work.

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