

# Electropolymerization of Nitrophenol Isomers in Various Aqueous Electrolytic Solutions

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This study focuses on the electrodeposition of 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol in either acidic, alkaline or neutral aqueous solutions. All the isomers have been electropolymerized using cyclic voltammetry (CV). A notable feature in all CV measurements was that the insulating polymer films deposited on gold electrodes ( $A = 0.02 \text{ cm}^2$ ) from solutions were revealed by the rapid drop in current measured, when compared to the original CV scans. Generally, the anodic oxidation potential for 3-nitrophenol was slightly lower than that for 2-nitrophenol and 4-nitrophenol electropolymerized from solutions of similar pH. Values of the molecular orbital energies of the HOMO and LUMO orbitals of the nitrophenol monomers in various ionization states were determined. Energy values were calculated and used to explain the electrochemistry of nitrophenol isomers. Electropolymerization of nitrophenol isomers was found to be most difficult in acid and easiest in basic medium. This was also confirmed by the calculated diffusion coefficients of the monomers. In conclusion, 3-nitrophenol showed the best electropolymerization performance, and 2-nitrophenol showed very poor coverage on the electrode surface.

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**Keywords:** Modified Electrodes; Thin Film; Oxidation; Diffusion.

## 1. INTRODUCTION

Electropolymerization is a well-known technique used for depositing a thin film of polymer on conducting substrates, for example on gold, by means of cyclic voltammetry.[1-5] Several researchers have performed electropolymerization on various derivatives of phenol to produce non-conducting polymers,[6-9] to protect surfaces from corrosion,[10] as membranes for biosensors,[11] or for waste water treatment.[12]

The electropolymerization of polyphenol derivatives has been extensively studied in the literature by several researchers. Samet *et.al.*[13] compared the electropolymerization of phenol

derivatives such as phenol, *o*-methoxyphenol and *o*-nitrophenol by cyclic voltammetry and optical microscopic techniques on gold and carbon steel electrodes. They could successfully prepare adherent polyphenol films using *o*-methoxyphenol to protect carbon steel against corrosion.[13]

Li *et. al.*[14] concluded that the electropolymerization of *p*-nitrophenyl-functionalized thiophene derivatives produced materials having the electronic properties of both polythiophene and nitrobenzene. Nitro groups exhibit a complex nature of the studied cyclic voltammetric curves in the obtained solid polymeric films.[14]

Bao *et. al.*[15] electrochemically coated polyphenol flakes on stainless steel samples in 0.1 mol dm<sup>-3</sup> phenol neutral solutions with an electrolyte composed of 0.1 mol dm<sup>-3</sup> sodium sulfate by cyclic voltammetry.[15] Pham *et. al.*[16] have proposed an electropolymerization mechanism of substituted phenols on steel electrodes. The electrochemical nature of the substituents and their positions are important factors in the stability of polymers. They concluded that the polymer film formation is quick when the *para* position of the hydroxyl group is free, whereas it cannot happen when the *para* and one of the *ortho* positions are barren.[16]

In previous works of this laboratory, we have studied the electropolymerization process of several non-conducting polymers that include poly-phenol derivatives, such as 1,2-dihydroxybenzene; 2-hydroxybenzyl alcohol; 1,3-dihydroxybenzene; 3-hydroxybenzyl alcohol; 1,4-dihydroxybenzene; 4-hydroxybenzyl alcohol; 2-aminophenol; 2-aminobenzyl alcohol; 3-aminophenol; and 3-aminobenzyl alcohol, from aqueous solutions at various pH values.[3, 4, 17-19] It was presented that the rapid drop in current values was indicative of polymeric film growth on gold working electrodes, as observed in cyclic voltammetry.

As far as our current knowledge goes, the electropolymerization of the nitrophenol isomers has not been extensively studied in the literature, and hence the need to conduct comprehensive electrochemical research in various aqueous media to enrich our knowledge of these compounds. Most of the papers in the existing literature focus on the determination of nitrophenol isomers in different samples environmentally or industrially.[20-23]

In the present research, we utilize nitrophenol isomers to deposit insulating non-conducting polymers on gold electrodes by electropolymerization. Consequently, monomer precursors are dissolved in solutions of different pH values that vary between acidic, neutral and basic mediums. When current was applied to these solutions, thin layers of the polymer could be synthesized and deposited on a wide range of conducting and semiconducting surfaces, e.g. gold. Thus, in this paper the electrochemical behavior of 2-nitrophenol, 3-nitrophenol and 4-nitrophenol is compared and contrasted, and a link is established between anodic oxidation potentials, calculated energies of the HOMO and LUMO molecular orbitals and the effect of pH/pKa on the entire electropolymerization process.

## 2. EXPERIMENTAL

### 2.1. Materials and reagents

All chemicals were used as received. 2-nitrophenol (>98%), 3-nitrophenol (>98%), 4-nitrophenol (>99%), potassium ferrocyanide trihydrate (>98%), potassium chloride (99%), and potassium ferricyanide (>98%) were all purchased from Alfa Aesar, Germany. Sulfuric acid (95-98%)

and sodium hydroxide (98%) were procured from PRS, Panreac, Spain. All aqueous solutions were prepared using deionized water from a Milli-pore Milli-Q system (resistivity= 18.2 M $\Omega$  cm).

## 2.2. Film Preparation

The electropolymerization experiments were conducted using a three electrode glass cell as previously described.[18] In brief, an EZstat Pro-potentiostat manufactured by NuVant Systems Inc. (IN, USA) and equipped with an EZware 2013 V7 analyzing software was used throughout the course of this work. At the beginning of each electrochemical experiment, the working electrode was mechanically polished for two minutes using the suspended solution of 0.05 $\mu$ m alumina performed on polishing pads (polishing kit number: PK-4) purchased from BASi Preclinical services (IN, USA). A platinum coiled wire (230 mm) mounted in a CTFE cylinder was used as the counter electrode. All the electrodes were supplied by BASi (IN, USA).

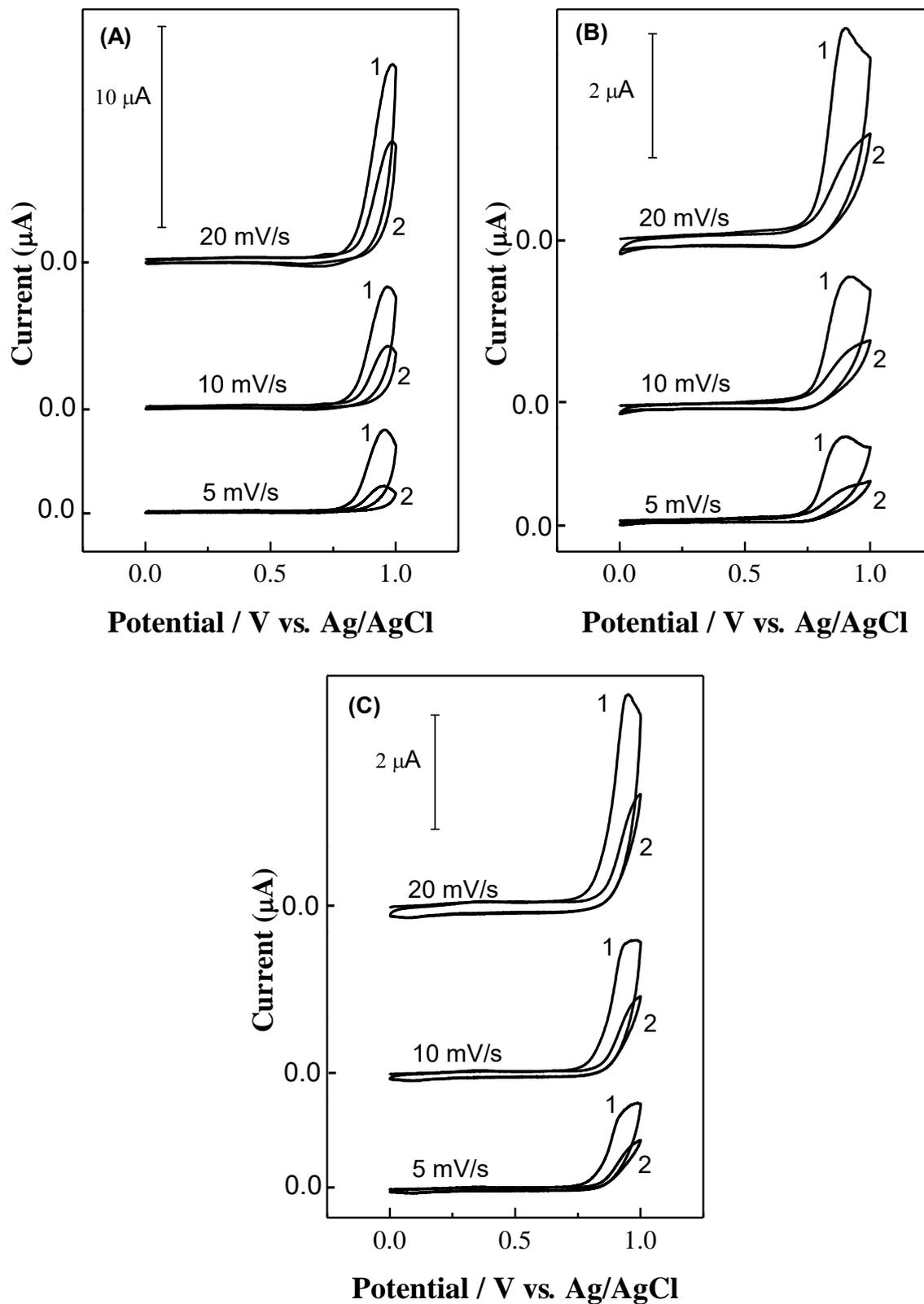
The polished gold electrode was immediately flushed with excess deionized water to remove any remaining alumina deposits. All the polished electrodes were tested before usage by performing cyclic voltammetry runs operated between -0.2 V and 0.6 V, in a solution of 5.0 mmol dm<sup>-3</sup> K<sub>3</sub>Fe(CN)<sub>6</sub>/ K<sub>4</sub>Fe(CN)<sub>6</sub> consisting of 0.1 mol dm<sup>-3</sup> KCl vs. (Ag/AgCl, 3.0 mol dm<sup>-3</sup> KCl) at a sweep rate of 20 mV s<sup>-1</sup> for four sweeps of applied potential.[18]

All the nitrophenol isomers used in this study were electropolymerized at 1.6 mm diameter polished gold electrodes ( $A= 0.02$  cm<sup>2</sup>). Based on the supporting electrolyte, several solutions of 0.1 mol dm<sup>-3</sup> 2-nitrophenol, 0.1 mol dm<sup>-3</sup> 3-nitrophenol and 0.1 mol dm<sup>-3</sup> 4-nitrophenol were prepared separately by using either KCl (0.1 mol dm<sup>-3</sup>, neutral solution), H<sub>2</sub>SO<sub>4</sub> (0.1 mol dm<sup>-3</sup>, acid solution) or NaOH (0.1 mol dm<sup>-3</sup>, basic solution). The prepared solutions were then electropolymerized vs. (Ag/AgCl, 3.0 mol dm<sup>-3</sup> KCl) by applying the sweeping potential between 0.0–1.0 V for basic and neutral solutions, and for acidic samples the applied potential was 0.0–1.2 V. Various scan rates were used, such as 5, 10 and 20 mV s<sup>-1</sup> for six sweeps of applied potential. It meant that the electrochemical polymerization was performed by using cyclic voltammetry in the mentioned potential region using six cycles. At the end of each electropolymerization experiment, all the modified electrodes were tested in a solution of 5.0 mmol dm<sup>-3</sup> K<sub>3</sub>Fe(CN)<sub>6</sub>/ K<sub>4</sub>Fe(CN)<sub>6</sub> consisting of 0.1 mol dm<sup>-3</sup> KCl vs. (Ag/AgCl, 3.0 mol dm<sup>-3</sup> KCl) at a sweep rate of 20 mV s<sup>-1</sup> for four sweeps of applied potential. This necessary step was conducted to ensure that the polymer film was fully deposited at the electrode surface.

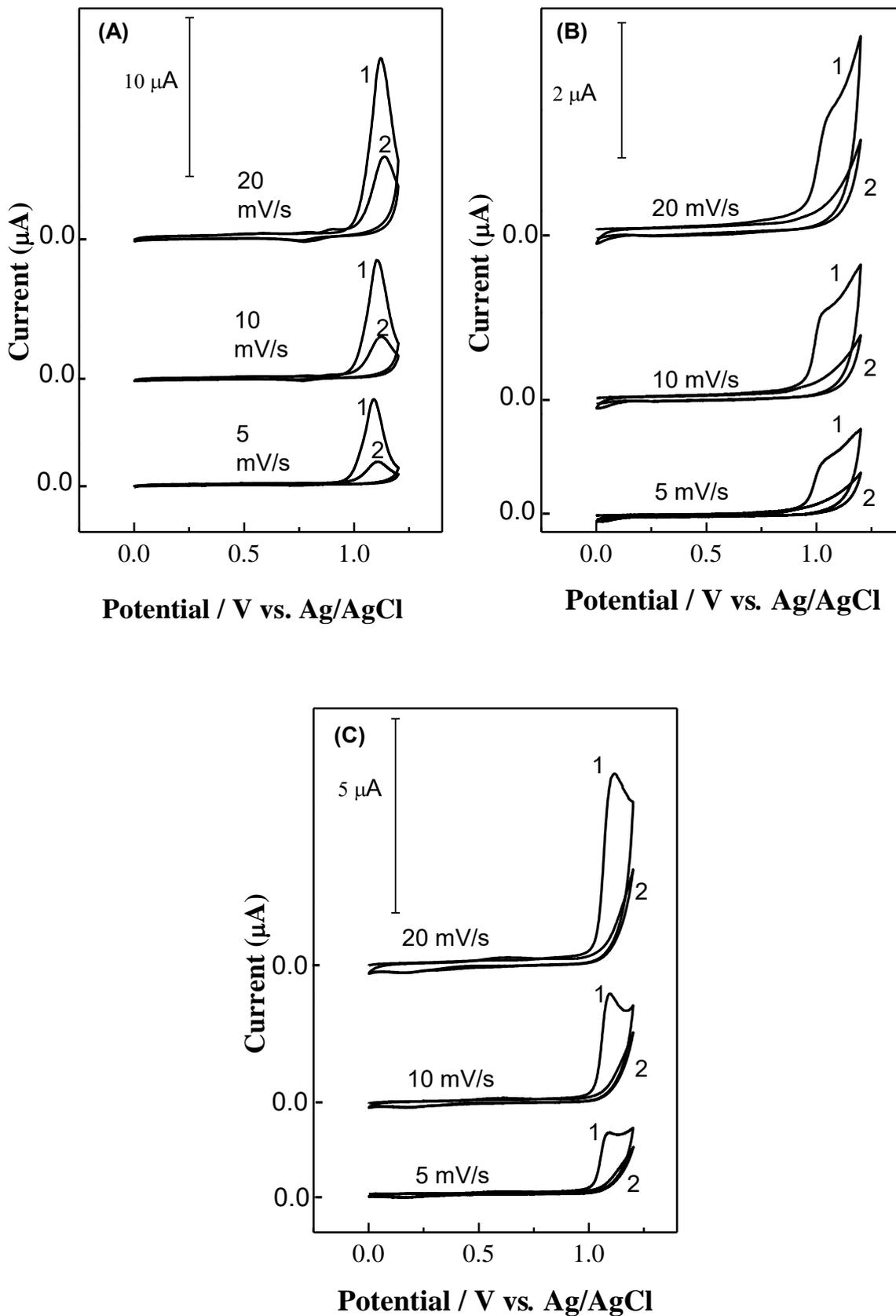
## 2.3. Molecular Orbital Calculations

In the present study, Spartan 14 (V1.1.4) software, the well-known molecular modelling suite, has been used here to calculate the HOMO and the LUMO frontier molecular energies.[18] At restricted Hartree–Fock level using HF/6-311G\* model, all the neutral and ionic structures built followed by the geometrical optimization were calculated and modelled at the ground state.[18]

## 3. RESULTS AND DISCUSSION



**Figure 1.** First two cyclic voltammograms of  $0.1 \text{ mol dm}^{-3}$  nitrophenol isomers that have been electropolymerized from neutral solutions at pH equal to 7.0 ( $0.1 \text{ mol dm}^{-3}$  KCl): (a) 2-nitrophenol, (b) 3-nitrophenol, and (c) 4-nitrophenol.



**Figure 2.** First two cyclic voltammograms of 0.1 mol dm<sup>-3</sup> nitrophenol isomers that have been electropolymerized from sulfuric acid (0.1 mol dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub>): (a) 2-nitrophenol, (b) 3-nitrophenol, and (c) 4-nitrophenol.

Fig. 1 presented the cyclic voltammogram (CV) scans for the first two cycles of 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol in neutral solutions ( $\text{pH} = 7.0$ ) recorded at different scan rates of 5, 10, and 20  $\text{mV s}^{-1}$ . A general inspection of Fig. 1 shows that the CV curves for all isomers exhibited only anodic oxidation peaks ranging from 0.75 to 1.0 V. This is indicative of irreversible oxidation reaction of nitrophenol monomer at the surface of the electrode. The current of anodic peaks was decreased approximately 22-fold during the successive sweeps of potential. This behavior is explained by the deposition of a passivating layer of polynitrophenol on the electrode surface.

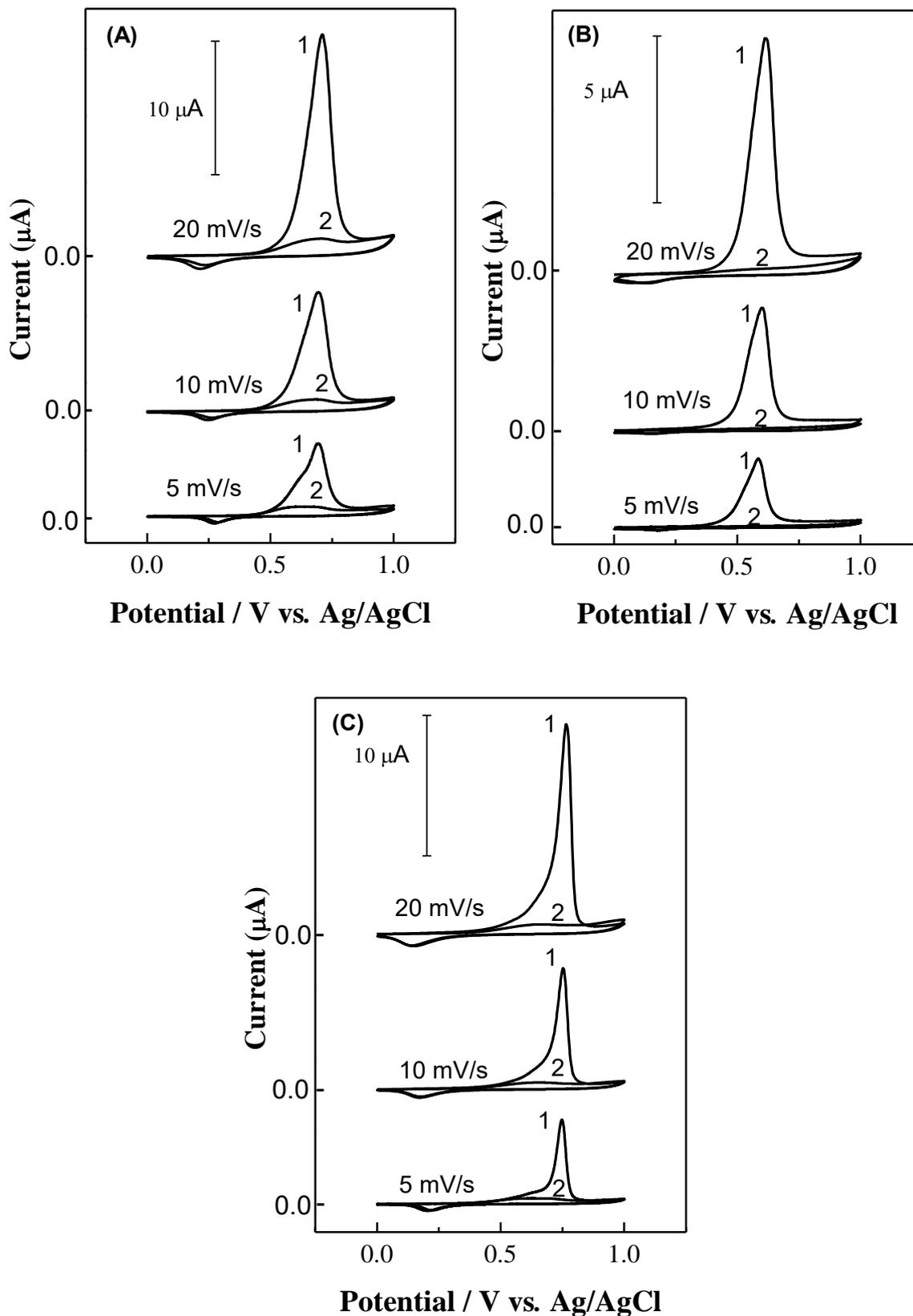
Fig.1a shows that the potential values of onset and peak for 2-nitrophenol were 0.78 and 1.00 V, respectively. These values were slightly higher when compared with 0.75 and 0.89 V for 3-nitrophenol (Fig. 1b) and 0.77 and 0.95 V for 4-nitrophenol (Fig. 1c). All isomers in question seem to follow an electropolymerization reaction, as indicated by the fact that the current is decreased clearly in the second CV scan.

At  $\text{pH} \leq 7$ , the oxidation mechanism of 3-nitrophenol involves the removal of two electrons and one  $\text{H}^+$  ion from the hydroxyl group. Three possible resonance structures could be drawn having a carbon atom that is electron deficient, a so-called phenoxonium ion, either at the ortho or para positions of the benzene ring. The phenoxonium ion will be stabilized by the resonance structures formed. In a similar approach to the monomer, the dimers are formed between the intermediate phenoxonium ions. They are further oxidized to form oligomers through a C-C coupling.[24] Finally, a polymer layer could be deposited at the electrode surface, as seen in Fig. 1b.

A similar mechanism has been proposed for the electrochemical oxidation of 2-nitrophenol and 4-nitrophenol at  $\text{pH} \leq 7$ . The phenoxonium ion will be formed at the ortho or the para and not on the meta position. In this case, the nitro group could be involved in the resonance structures, and this will offer the para position priority. Hence, the stabilized phenoxonium ion is caused by both the resonance and the inductive effect at their maximum level. This phenomenon is responsible for lowering the pKa values of 2-nitrophenol and 4-nitrophenol, which behave as better acids compared to 3-nitrophenol.

Fig.2 illustrates that all the nitrophenol isomers prepared in acidic solutions of  $0.1 \text{ mol dm}^{-3}$  of  $\text{H}_2\text{SO}_4$  exhibit electropolymerization, as clearly indicated by the CV curves of the two cycles. In Fig. 2a, two peaks are observed in the CV curves. However, the maximum current peaks are found to be dependent on the scan rate applied. For example, in the first cycle, the maximum current peak is 2-fold greater (at  $20 \text{ mV s}^{-1}$  scan rate) and 4-fold (at  $5 \text{ mV s}^{-1}$  scan rate) when compared with the same in the second cycle. On the other hand, peaks are not observed in Fig. 2b and 2c. From these figures, one can inspect that the levels in the second cycle are 4-fold and 6-fold smaller than that in the first cycle for 3-nitrophenol and 4-nitrophenol, respectively. Onset peak values and peak potentials for 2-nitrophenol are 0.9 and 1.1 V, respectively. These values are smaller than 0.7 and 1.0 V for 3-nitrophenol (Fig.2b), but nearly equivalent to 1.0 and 1.1 V for the oxidation of 4-nitrophenol (Fig.2c). The measured pH value for all the nitrophenol prepared in acidic solutions was 1.4.

Fig. 3 presents the CV curves of the first two cycles that lead to the electropolymerization of nitrophenol isomers prepared in basic aqueous solutions of  $0.1 \text{ mol dm}^{-3}$  NaOH. In the second cycle, anodic oxidation peak was absent from all the CV scans. This behavior is explained by the deposition of a strong passivating layer of polynitrophenol on the electrode surface.



**Figure 3.** First two cyclic voltammograms of  $0.1 \text{ mol dm}^{-3}$  nitrophenol isomers that have been electropolymerized from sodium hydroxide ( $0.1 \text{ mol dm}^{-3}$ ): (a) 2-nitrophenol, (b) 3-nitrophenol, and (c) 4-nitrophenol.

In Fig. 3b, 3-nitrophenol showed the highest difference between the two cycles by approximately 38-fold ( $20 \text{ mV s}^{-1}$ ), 53-fold ( $10 \text{ mV s}^{-1}$ ), and 40-fold ( $5 \text{ mVs}^{-1}$ ). The difference in the peak currents between the two cycles for 2-nitrophenol was the lowest by approximately 10-Fold (Fig. 3a), whereas for the same in 4-nitrophenol it was approximately 24-fold (e.g. at  $20 \text{ mV s}^{-1}$ ) (Fig. 3c).

The onset and peak potentials for 2-nitrophenol were determined at 0.40 and 0.70 V, respectively, as seen in Fig. 3a. These values were slightly similar compared to the values of 0.30 and 0.75 V for 3-nitrophenol (Fig. 3b) and for the oxidation of 4-nitrophenol of 0.50 and 0.60 V (Fig. 3c). The measured pH values in this laboratory for 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol prepared in basic solutions are 10.2, 11.2 and 10.8, respectively.

In basic media, 2-nitrophenol, 3-nitrophenol and 4-nitrophenol are ionized when the H atom on the hydroxyl group is deprotonated to phenates by losing  $\text{H}^+$  from the hydroxyl group on the benzene ring. The phenate ion will undergo oxidation upon electron removal to form a phenoxy radical represented by three different possible resonance species.

After the anodic oxidation of 3-nitrophenol occurred, the resonance structures between the three possibilities will stabilize the radical formed. We believe that the nitro group of 3-nitrophenol does not contribute to the polymerization process, as there are no radicals that will be end up on the meta position where the nitro group is located. In this case, in the mechanism of 3-nitrophenol the phenoxy radical is stabilized by the inductive effect only.

The story is different in the oxidation mechanism of 2-nitrophenol and 4-nitrophenol at  $\text{pH} > 7$ . In 2-nitrophenol, the phenoxy radicals will be formed at the ortho or the para and not on the meta position. In this case, the nitro group could be involved in the resonance structures, and this makes the para position a more resonating stabilized point. This will lead to a lower pKa value, because a more resonating stabilized conjugate base will result in a better acidic compound. Hence, the stabilized phenoxy radicals are caused by both the resonance and the inductive effect at their maximum effect.

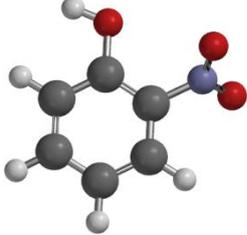
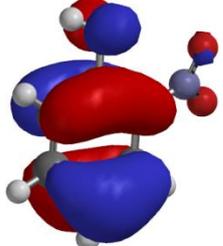
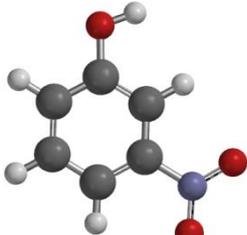
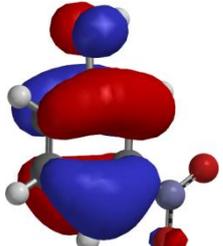
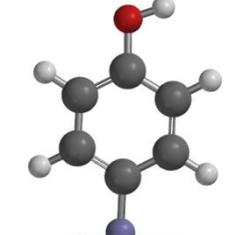
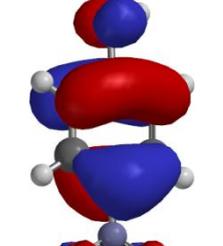
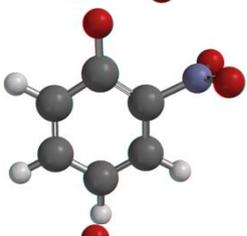
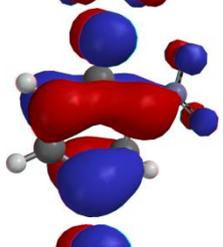
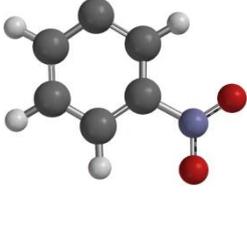
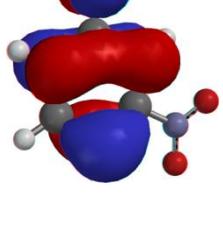
In a similar manner to the monomer, the dimers are formed between the intermediates radicals and they are further oxidized to form oligomers. In theory, there are several coupling possibilities, but practically it is the so-called head to tail (C-O-C) coupling that is virtually common.[24] Finally, a polymer layer deposit will be obtained at the electrode surface.

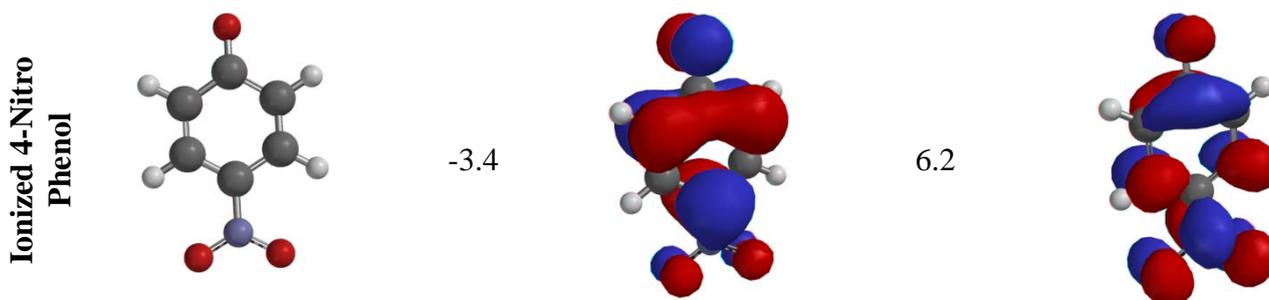
On the other hand, in 4-nitrophenol, the phenoxy radical is stabilized by both the resonance and the inductive effect at their minimum outcome. Therefore, based on the stability of the phenoxy radicals, the 2-nitrophenol seems to be more acidic than 4-nitrophenol, which in turn will be more acidic compared to the 3-nitrophenol. However, due to an intramolecular hydrogen bonding in 2-nitrophenol and the steric hindrance observed, it becomes difficult to remove the hydrogen atom from the structure of the isomer 2-nitrophenol. In this case, 2-nitrophenol seems to be less acidic than 4-nitrophenol.[25] At this point, the final order of decreasing acidity is 4-nitrophenol > 2-nitrophenol > 3-nitrophenol > phenol.

Table 1 presents the calculated energies of the HOMO and LUMO of the uncharged molecules at  $\text{pH} = 7$ . The calculated HOMO and LUMO values for 2-nitrophenol and 4-nitrophenol are quite close, explaining the slightly similar acidic behavior as observed above. The ionized 3-nitrophenol has the lowest energy values of the HOMO and LUMO compared to the other isomers.

Based on the literature, pKa value recorded at 25°C of 2-nitrophenol is 7.23, 3-nitrophenol is 8.36 and 4-nitrophenol is 7.15.[25] It is well known, that the higher the pKa the more basic the compound is, and one can prove this as described in the above paragraphs. These observations agree with the acidity order as observed above.

**Table 1.** Geometrical plots and the calculated energy values of the HOMO and LUMO molecular orbitals for 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol.

|                        |   | E_HOMO<br>(eV) |   | E_LUMO<br>(eV) |
|------------------------|---|----------------|---|----------------|
| 2-Nitro Phenol         |    | -9.5           |    | 1.9            |
| 3-Nitro Phenol         |   | -9.4           |   | 1.4            |
| 4-Nitro Phenol         |  | -9.6           |  | 1.8            |
| Ionized 2-Nitro Phenol |  | -3.3           |  | 6.4            |
| Ionized 3-Nitro Phenol |  | -2.9           |  | 5.8            |



The electrochemical behavior of all the modified electrodes with polynitrophenol films prepared in different pH solutions by CV using a scan rate of  $5\text{ mV s}^{-1}$  is presented in Fig. 4. Fig. 4a presents a typical CV curve of the bare working gold electrode tested in equal concentrations of  $5.0\text{ mmol dm}^{-3}$   $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  solution ( $0.1\text{ mol dm}^{-3}$  KCl as the supporting electrolyte). Peaks of the oxidation (+260 mV) and reduction (+170 mV) are observed in Fig. 4a.

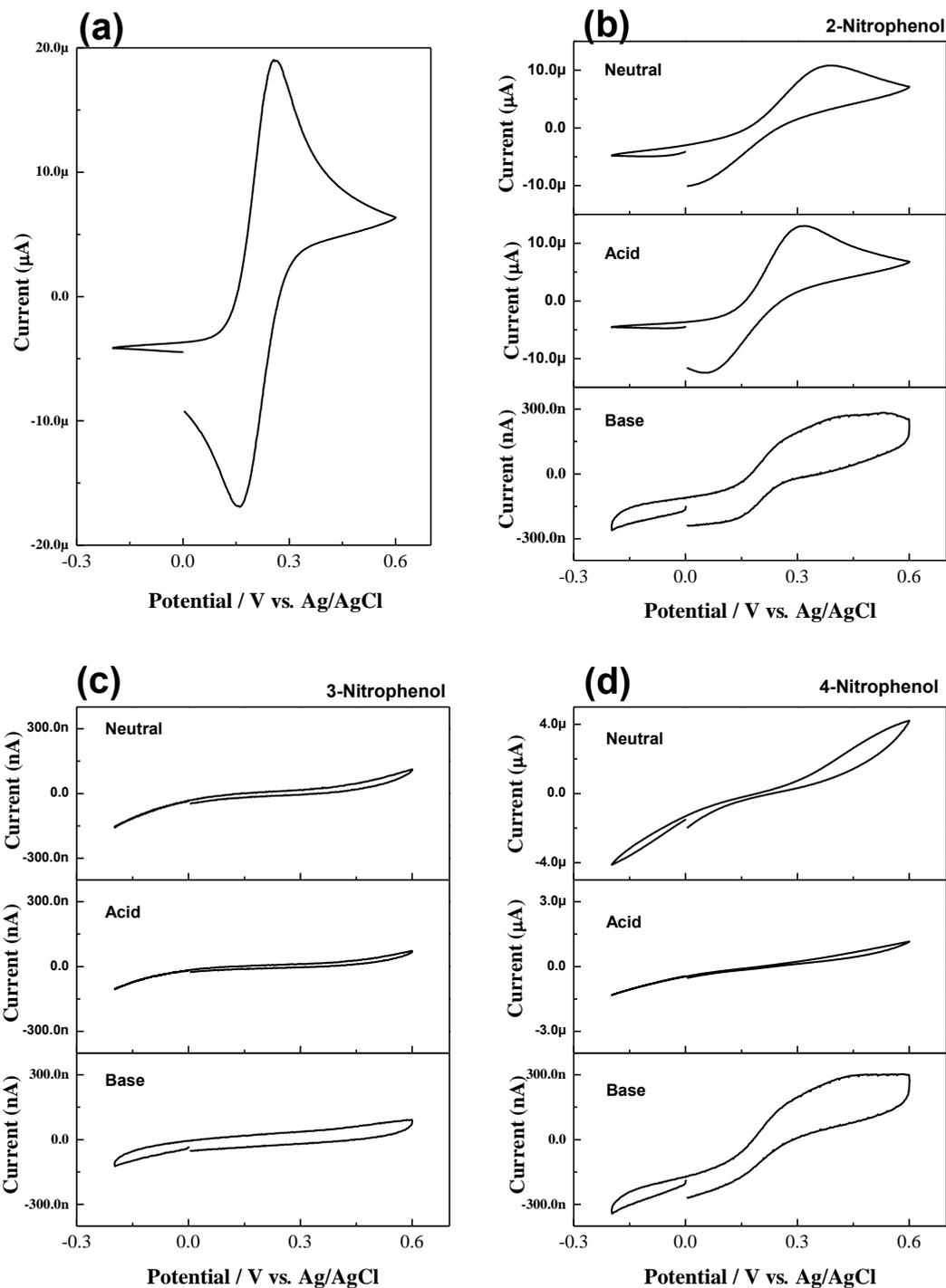
Franco *et. al.* studied the electropolymerization of 3-aminophenol in acidic and basic media.[26] They tested their polyaminophenol modified electrodes in the presence of the aqueous  $5.0\text{ mmol dm}^{-3}$   $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  redox couple. They contrasted the signal of graphite electrode with the bare electrode with the modified ones. The current peaks on the modified electrodes diminished. They found that the inclination angle and area of the peaks decreased as well. This suggested a higher resistance of the system. This reflects the covering of the electrode surface by insulator polymeric film.[26]

The deposition process of the polymer film on the electrode surface was confirmed in Fig. 4b-d as per the method described.[26] These figures presented the CV curves tested in  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  redox couple of the modified electrodes with different nitrophenol isomers that have been electropolymerized from different aqueous pH solutions.

The most remarkable feature of the CVs is that the current has dropped piercingly into the nano ampere range and the smooth peak features have totally vanished from the curves. This was clearly seen in all traces of Fig. 4c and in basic medium trace of Fig.4b and 4c, as a result of the electropolymerization and thin film formation of 3-nitrophenol isomer from different pH solutions.

Samet *et. al.*[13] studied the electropolymerization of  $5.0\text{ mmol dm}^{-3}$  of 2-nitrophenol in  $0.5\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  by CV at a scan rate of  $50\text{ mV s}^{-1}$ . During the reverse scan in their CV results, a well-defined peak was observed. They claimed that this peak is related to the reduction of the produced oxidation products of 2-nitrophenol. They concluded that the electropolymerization reaction in that case is not significant.[13] There is no reduction peak observed in all the electropolymerization CV scans (Fig. 1 and 2) in either cycle, although a higher concentration of the monomers has been used here of  $0.1\text{ mol dm}^{-3}$  with a 20-fold slower scan rate between 20 to  $5\text{ mV s}^{-1}$  compared with Samet *et. al.*[13]

In the presence of  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  redox couple (Fig. 4b), CV traces of 2-nitrophenol that has been electropolymerized from neutral and acidic solutions showed both oxidation and reduction peaks as seen in Fig.4a. In neutral, the oxidation reduction peaks were at +400 mV and 0 mV, respectively, whereas in acidic medium, the oxidation reduction peaks were at +320 mV and 50 mV, respectively.



**Figure 4.** Cyclic voltammogram of the bare gold electrode ( $A= 0.02 \text{ cm}^2$ ) and the modified gold electrodes with electropolymerized nitrophenol isomers, ( $0.1 \text{ mol dm}^{-3}$ ,  $5 \text{ mVs}^{-1}$  scan rate) in aqueous solution containing equal concentrations of  $5.0 \text{ mmol dm}^{-3} \text{K}_3\text{Fe}(\text{CN})_6/ \text{K}_4\text{Fe}(\text{CN})_6$  ( $0.1 \text{ mol dm}^{-3} \text{KCl}$ ),  $20 \text{ mVs}^{-1}$ . (a) Gold electrode without film and the modified electrodes at (b)  $0.1 \text{ mol dm}^{-3}$  of 2-nitrophenol in neutral solutions ( $0.1 \text{ mol dm}^{-3} \text{KCl}$ ), acid ( $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ ), and base ( $0.1 \text{ mol dm}^{-3} \text{NaOH}$ ), (c) same as in (b) using 3-nitrophenol isomer, (d) same as in (b) using 4-nitrophenol isomer. For all experiments in this work,  $0.1 \text{ mol dm}^{-3}$  was used in the preparation of all the nitrophenol isomers from aqueous solutions.

The shift in peak positions showed the irreversibility of the process when compared with the CV of the polished bare electrode. This change in electrochemical behavior can be simply explained by a passivation of the electrode surface that prevents reduction of ferricyanide as opposed to electrostatic repulsion.

In Fig. 4d, CVs of both neutral and acid media seem to behave similar to those in Fig. 4c. They experienced a drop in anodic current in the micro-ampere range between 1-3  $\mu\text{A}$  without a distinct inclination of angle peaks. This phenomenon is related to the electropolymerization of nitrophenol isomers, as an insulating polymer layer was electrochemically synthesized at the surface of the gold electrode.

Table 2 shows the diffusion coefficients for nitrophenol isomers measured from the first cycle of the electropolymerization CVs at different scan rates ranging from 5 to 45  $\text{mV s}^{-1}$ . It was found that with increasing scan rate, the peak current ( $i_p$ ) increased linearly with the square root of the potential scan rate ( $v^{1/2}$ ). This confirms that the electropolymerization of nitrophenol isomers is a linear diffusion controlled process. The diffusion coefficients are measured using Randles–Sevcik Eq. 1:[27, 28]

$$I_p = (2.69 \times 10^5) n^{2/3} A \sqrt{D} \sqrt{v} C \dots \text{equation 1}$$

Where:  $I_p$ : the peak current,  $n$ : the number of electrons,  $A$ : the surface area of the working electrode,  $D$ : the diffusion coefficient of the electroactive species,  $v$ : the scan rate of voltammograms, and  $C$ : the bulk concentration of the electroactive species.

**Table 2.** Calculated values of diffusion coefficients.

| Nitrophenol Isomers | Diffusion Coefficients<br>$\text{cm}^2 \text{s}^{-1} \times 10^{-5}$ |         |          |
|---------------------|--|---------|----------|
|                     | Acid   | Neutral | Alkaline |
| 2-Nitrophenol       | 4.0  | 6.2     | 2.2      |
| 3-Nitrophenol       | 158.0  | 53.1    | 13.3     |
| 4-Nitrophenol       | 26.3   | 43.9    | 2.8      |

By comparing the results between Fig. 4 and Table 2, 3-nitrophenol has the highest diffusion coefficients among the isomers studied. The variation in the diffusion coefficients of the isomers at the different pH values used in this study is in the order of 40-fold. The calculated diffusion coefficient values in alkaline aqueous solutions for 2-nitrophenol and 4-nitrophenol are approximately the same but the value for 3-nitrophenol is approximately ten times higher with an increase of a 10-fold factor in 3-nitrophenol. Accordingly, the electropolymerization process is favored in basic solutions. This appears to assist the monomer tendency to form a polymeric thin film as presented above.

#### 4. CONCLUSION

This paper demonstrates that the electrodeposition of polymeric films consequential to 2-nitrophenol, 3-nitrophenol, or 4-nitrophenol isomers at the surface of gold electrodes is feasible. It was concluded that the electropolymerization process can be harvested from different pH media such as acidic, alkaline or neutral aqueous solutions. With pH increase, the cyclic voltammetric measurements revealed that anodic oxidation, and polymerization of 2-nitrophenol, 3-nitrophenol or 4-nitrophenol becomes increasingly favored. Hence, the anodic potential for 3-nitrophenol is slightly lower than that for the corresponding values of 2-nitrophenol and 4-nitrophenol for solutions of similar pH.

In conclusion, the electropolymerization of nitrophenol isomers was found to be most difficult in acid and easiest in alkaline aqueous medium. This was also confirmed by the calculated diffusion coefficients of the monomers. In alkaline aqueous solutions, the calculated diffusion coefficient values are approximately the same for 2-nitrophenol and 4-nitrophenol, with the value for 3-nitrophenol being approximately ten times higher. Indeed, 3-nitrophenol has the highest diffusion coefficients among the isomers. Therefore, 3-nitrophenol showed the best electropolymerization performance, and 2-nitrophenol showed very poor coverage on the electrode surface.

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