

EVALUATION OF THE ELECTRO-CATALYTIC OXIDATION OF ASCORBIC ACID, USING A PLATINUM ELECTRODE MODIFIED WITH POLY-3-METHYLTHIOPHENE

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ABSTRACT

This study investigated the oxidation of ascorbic acid using a clean platinum electrode coated with a film of poly-3-methylthiophene, called a modified electrode. The films were grown using the chronoamperometric technique and the electrochemical measurements were taken using the cyclic voltammetry technique. We analyzed the anodic peak current and the anodic peak potential using the platinum electrode with and without the film, and in the presence and absence of ascorbic acid. We also investigated the effect of ascorbic acid concentration, the effect of scan rate and the effect of the pH of the solution on the parameters of anodic peak. The results show that the anodic current peak increases and the potential of anodic peak shifts to a more negative value when compared with the clean electrode. We also observed that the anodic peak current increases as the concentration of ascorbic acid, the scan rate and the pH increase. The anodic peak potential shifts to more positive values as the concentration of ascorbic acid and the scan rate increase, while it shifts to more negative values as the pH of the solution increases.

KEYWORDS: electrochemistry, ascorbic acid, poly-3-methylthiophene.

AVALIAÇÃO DA OXIDAÇÃO ELECTRO-CATALÍTICA DE ÁCIDO ASCÓRBICO, USANDO UM ELETRODO DE PLATINA MODIFICADO COM POLI-3-METILTIOFENO.

RESUMO

Nesse trabalho investigou-se a oxidação do ácido ascórbico utilizando um eletrodo de platina limpo e coberto com um filme de Poli-3-metiltiofeno, chamado eletrodo modificado. Os filmes foram crescidos pela técnica da cronoamperometria e as medidas eletroquímicas foram realizadas pela técnica da voltametria cíclica. Foram analisados a corrente de pico anódico e o potencial de pico anódico utilizando o eletrodo de platina sem filme e com o filme na presença e na ausência de ácido ascórbico. Foram investigados também o efeito da concentração de ácido ascórbico, o efeito da velocidade de varredura, e o efeito do pH da solução nos parâmetros de pico anódico. Os resultados mostraram que o pico de corrente anódica aumenta e o potencial de pico anódico se desloca para valores mais negativos quando comparado com o eletrodo limpo e o eletrodo modificado com poli-3-metiltiofeno. Verificou-se também que corrente de pico anódico aumenta com o aumento da

concentração de ácido ascórbico, com o aumento da velocidade de varredura e com o aumento do pH. Já o potencial de pico anódico, se desloca para valores mais positivos com o aumento da concentração de ácido ascórbico, com a velocidade de varredura, e se desloca para valores mais negativos com o aumento do pH da solução.

PALAVRAS CHAVES: eletroquímica, ácido ascórbico, poli-3-metil-tiofeno.

1. INTRODUCTION

Ascorbic acid is an essential vitamin in our diet. It is a powerful anti-oxidant and therefore helps prevent infectious diseases (HAMRICK et al 2008). Naturally present in many vegetables and fruits, it is added to various food products during their industrial processing in order to avoid undesirable alterations to the characteristics of the product, such as color, taste and smell (GARDNER, 2000). Due to its biological and technological significance, the food and biochemical industries have great interest in the development of routine, reliable methods for the analysis of ascorbic acid. Other than traditional methods such as chromatography (KISHIDA et al, 1992), spectrophotometry (MOESLINGER et al, 1995), iodometry (ANDRADE et al, 2002) and others, electro-chemical methods exist that have been increasingly used in recent decades (KULYS et al, 1991, RAOOF et al, 2005, XU et al, 2010). These methods basically consist of oxidizing ascorbic acid using metal electrodes (CISZEWSKI, 1999, POURNAGHI-AZAR et al, 2010), or vitreous carbon electrodes (ZHANG, 2001) or carbon paste electrodes (RAOOF et al, 2001).

The potential of electro-chemical oxidation of ascorbic acid is subject to the type of electrode. When a clean electrode is used, that is, without any film coating, the potential is very high, to the point that other undesired species are oxidized as well. A common technique consists in building a modified electrode so as to reduce the oxidation potential of ascorbic acid, resulting in a more selective analysis (SUN et al, 1998, PANDEY et al 2004, HU et al 2006, SHENG et al, 2006, XI et al, 2012). Thus, it is possible to build a device that is sensitive to a certain substance. Researchers concentrate their efforts on finding materials that ensure good selectivity, good reproducibility and good stability.

Other than reducing the oxidation potential, modified electrodes can also be used for the simultaneous determination of two or more compounds with electro-catalytic activity. Several articles have investigated ascorbic acid and dopamine (REIS et al, 2005, KUMAR et al, 2005, CHEN et al, 2006, HUANG et al, 2007). WANG et al, 2007, WEI et al, 2010). In most of these studies, which used different modified electrodes, ascorbic acid is modified at a lower potential than the dopamine oxidation potential. As these two compounds are present in many biological systems, it is possible to simultaneously determine the two using the cyclic voltammetry method.

Polymeric materials such as polyaniline, polypyrrole, polythiophene and others are commonly used as modifiers for electrodes (MOHADESI et al, 2007, LIN et al 2010). These are conductor polymers with redox properties that allow electro-chemical doping, that is, the intercalation of an ion that increases its catalytic property. Poly-3-methylthiophene is a polymer with conducting properties, a material with great potential for technological uses. From the electro-chemical point of view, this polymer is easily synthesized, has good stability and is reversible in the oxidation-reduction process. For this reason it has been widely used in the

construction of modified electrodes, used for the electro-oxidation of organic substances (ZHANG et al 2010, SUNDARI et al 2011). The purpose of our study was to build a modified electrode using a platinum electrode coated with a layer of poly-3-methylthiophene. This electrode is expected to lower the oxidation potential of ascorbic acid, becoming more selective to this compound. This would enable the future construction of a sensor to identify vitamin C in biological and alimentary systems.

2. MATERIALS AND METHODS

The reagents used were 3-methylthiophene (monomer) by Aldrich, acetonitrile by Synth, lithium perchlorate by Vetec and a Britton-Robinson buffer solution. This buffer solution is a mixture of sulphuric acid, boric acid and acetic acid, all at 0.04 mol/L; the desired pH is obtained by adding sodium hydroxide 0.2 mol/L. All reagents were used as they were acquired. The experiments were performed in an electro-chemical cell containing three electrodes: a platinum disc (area: 0.2 cm²) as working electrode, a reference silver/silver chloride electrode and a platinum plate as auxiliary electrode. The modified electrode was obtained by growing a film of poly-3-methylthiophene on the platinum surface. The films were grown in a solution of 0.1 mol/L of lithium perchlorate in acetonitrile containing 0.1 mol/L of the 3-methylthiophene monomer. For each film growth, the platinum electrode was cleaned with alumina paste until the surface became mirror-like. We used alumina 1.0, 0.3 and 0.05 μ m. After growth, the film was rinsed with de-ionized water and placed in another cell containing the buffer solution, for the measurements of cyclic voltammetry. The electro-chemical measurements were taken with the help of a potentiostat by Microquímica, model MQPG-01. The figures were registered using a computer with an interface MQI12/8 PQ.

3. RESULTS AND DISCUSSIONS

Figure 1 shows voltammograms obtained with the platinum electrode under different conditions: curve 1 (black) is the cycling performed with the clean electrode in the Britton-Robinson buffer solution with pH = 6; curve 2 (red) was obtained in the buffer solution containing 0.05 mol/L of ascorbic acid; curve 3 (green) is that of the electrode containing the film in the buffer solution without ascorbic acid and curve 4 (blue) refers to the electrode with the film of poly-3-methylthiophene containing 0.05 mol/L of ascorbic acid.

It can be seen that, for the clean electrode in the solution devoid of ascorbic acid (curve 1), only one cathodic peak appears at approximately 0.08 V, corresponding to the oxidation of water. When ascorbic acid is added to the solution (curve 2), a high anodic peak of current appears around 0.58 V, which, according to the literature (LYONS et al, 1991), corresponds to the oxidation of ascorbic acid at a clean platinum electrode versus a reference Ag/AgCl electrode. The return sweeping shows only the water oxidation peak. This means that the process is not reversible. In addition, the cathodic peak associated to water oxidation is reduced in the presence of ascorbic acid. This may be related to the adsorption of molecules of ascorbic acid on the surface of the electrode, preventing the interaction between platinum and the solvent molecules.

In the potential sweeping of the platinum electrode containing the film of poly-3-methylthiophene in the buffer solution without ascorbic acid, no anodic current peak appears; what is observed is a very wide peak in the return cathodic sweeping. The

absence of an anodic peak was expected due to the absence of ascorbic acid, while the wide cathodic peak is not yet well understood.

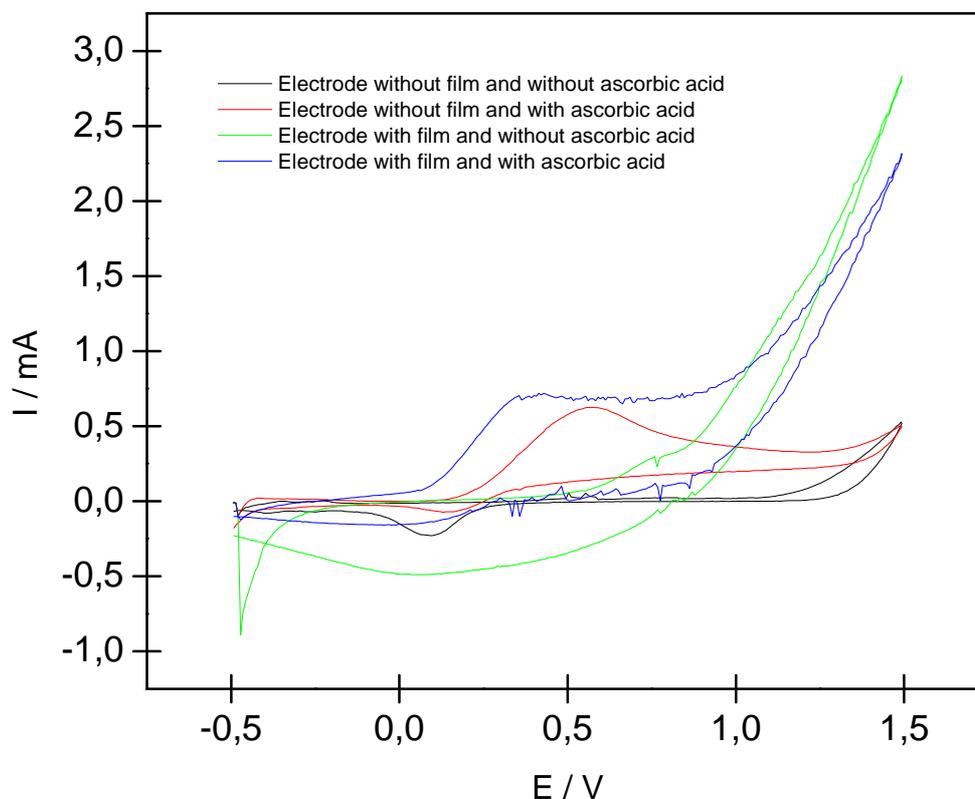


Figure 1: Voltammograms obtained under different conditions. The films of poly-3-methylthiophene were grown in an acetonitrile solution containing 0.1 mol/L of LiClO_4 and 0.1 mol/L of monomer and ambient temperature.

The last voltammogram of Figure 1, curve 4, corresponds to the electrode with the polymeric film in the presence of ascorbic acid. As can be observed, the anodic current peak increases and shifts to more negative potentials. This means that the electrode containing the film of poly-3-methylthiophene presents electro-catalytic activity to ascorbic acid. The increase of current peak indicates that a higher amount of species was oxidized, while the shift in potential shows higher facility in oxidizing these species. This shift of the potential to lower values is interesting, as it increases electrode selectivity.

3.1 Effects of ascorbic acid concentration

Figure 2 shows the voltammograms obtained through the variation of ascorbic acid concentration. As can be seen, within the concentration limits under study, the peak current suffers a marked increase as the concentration increases, and the peak potential shifts to more positive values. The increase in current shows that the modified electrode presents good sensitivity and stability in the presence of ascorbic acid. On the other hand, the shift of the peak potential value of ascorbic acid oxidation can be explained by the increase of ascorbic acid molecules on the surface of the electrode.

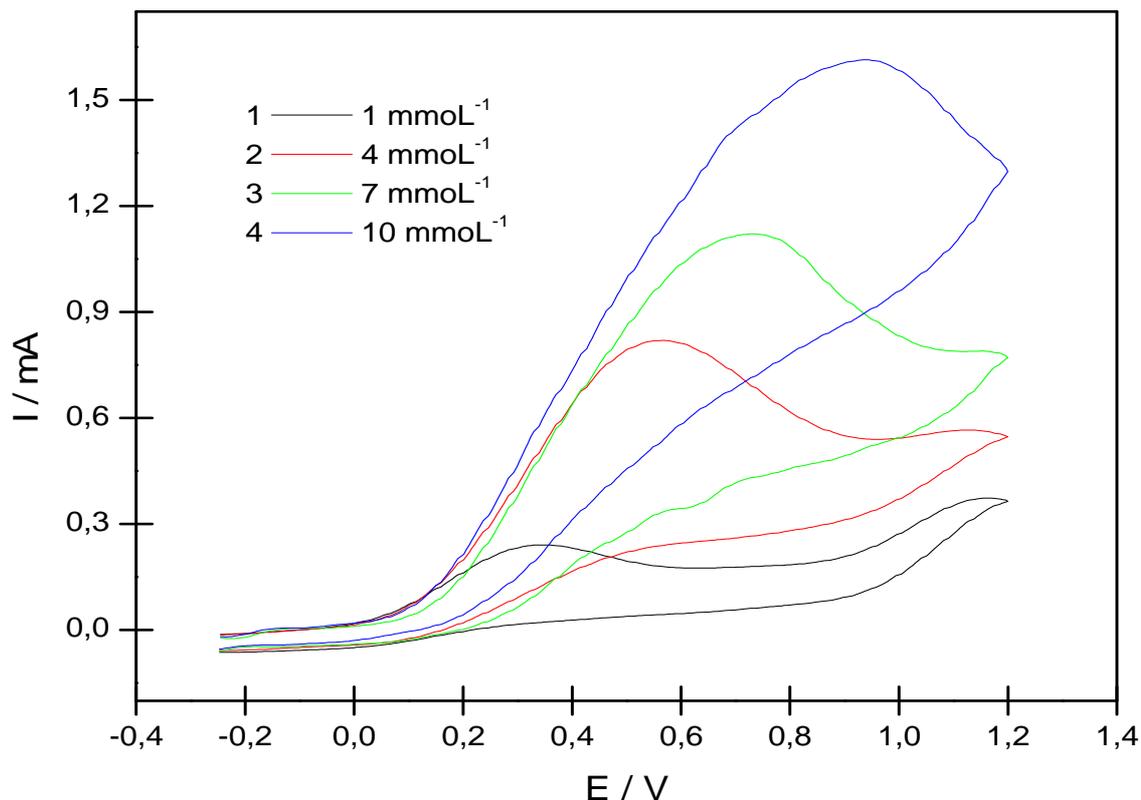


Figure 2: Voltammograms obtained from the modified electrode, in a buffer solution of pH = 6, varying the concentration of ascorbic acid. The films were grown in a 0.1 solution of lithium perchlorate in acetonitrile containing 0.1 molL⁻¹ of monomer.

In higher concentrations of ascorbic acid, the amount of molecules on the surface of the electrode will also be higher. As these molecules are oxidized, their concentration near the electrode falls, which means that in order to maintain surface concentration a large flow of species is generated from the middle of the solution to its surface.

The behavior of the anodic peak current with the concentration of ascorbic acid is illustrated in Figure 3. As can be observed, the increase is practically linear – a curve with a correlation coefficient of 0.994. This data confirms that within the concentration range under study the electrode shows good stability. The limit of detection has not yet been analyzed, but we know it is below the minimum figure presented here.

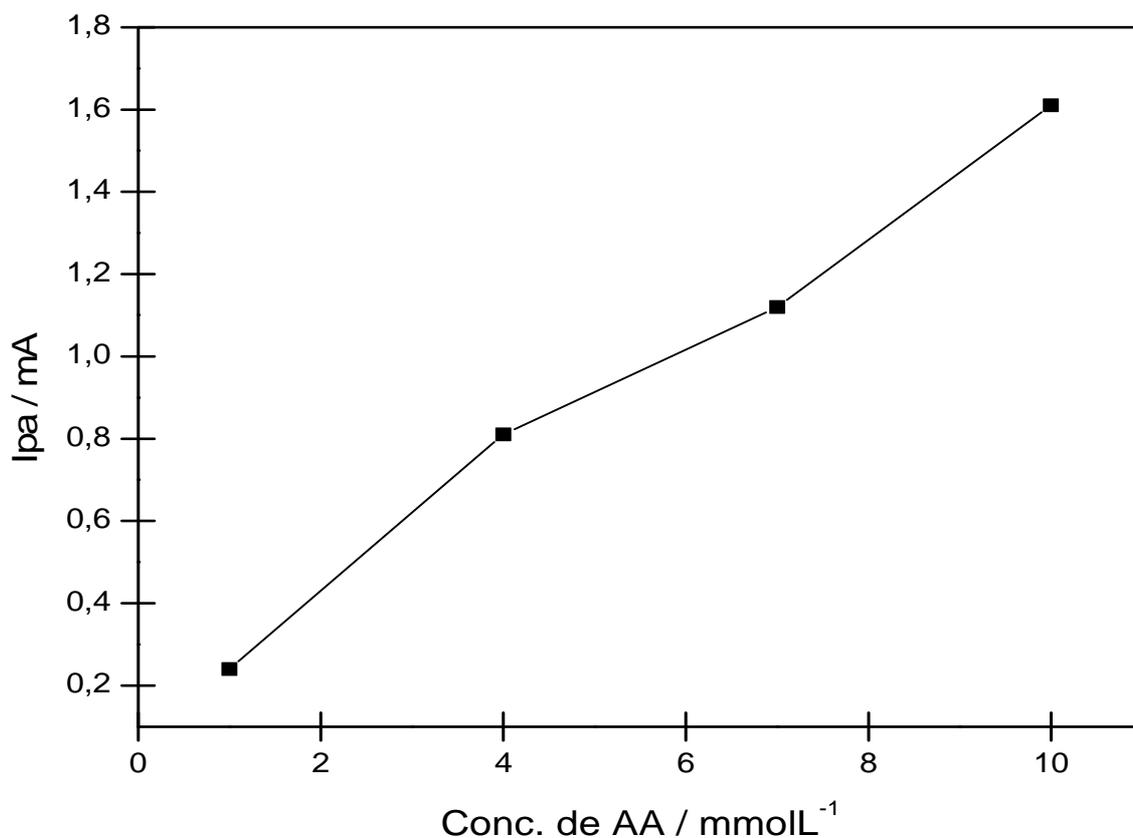


Figure 3: Values of cathodic peak current taken from the voltammograms shown in Figure 2, as a function of the concentration of ascorbic acid.

Figure 4 shows the variation of the peak potential with concentration. It can be observed that the shift of the potential to more positive values also has a linear behavior with the increase of the ascorbic acid concentration. The correlation coefficient is 0.997. The lower – more negative – the oxidation potential, the higher electrode selectivity will be. This can be explained by the fact that at high potentials other undesired species may also be oxidized, interfering with the results. Thus, this data indicate that the modified electrode under study has good selectivity, because the smaller oxidation potential is found at the lower concentration. Its limit of detection will probably be even more negative in potential.

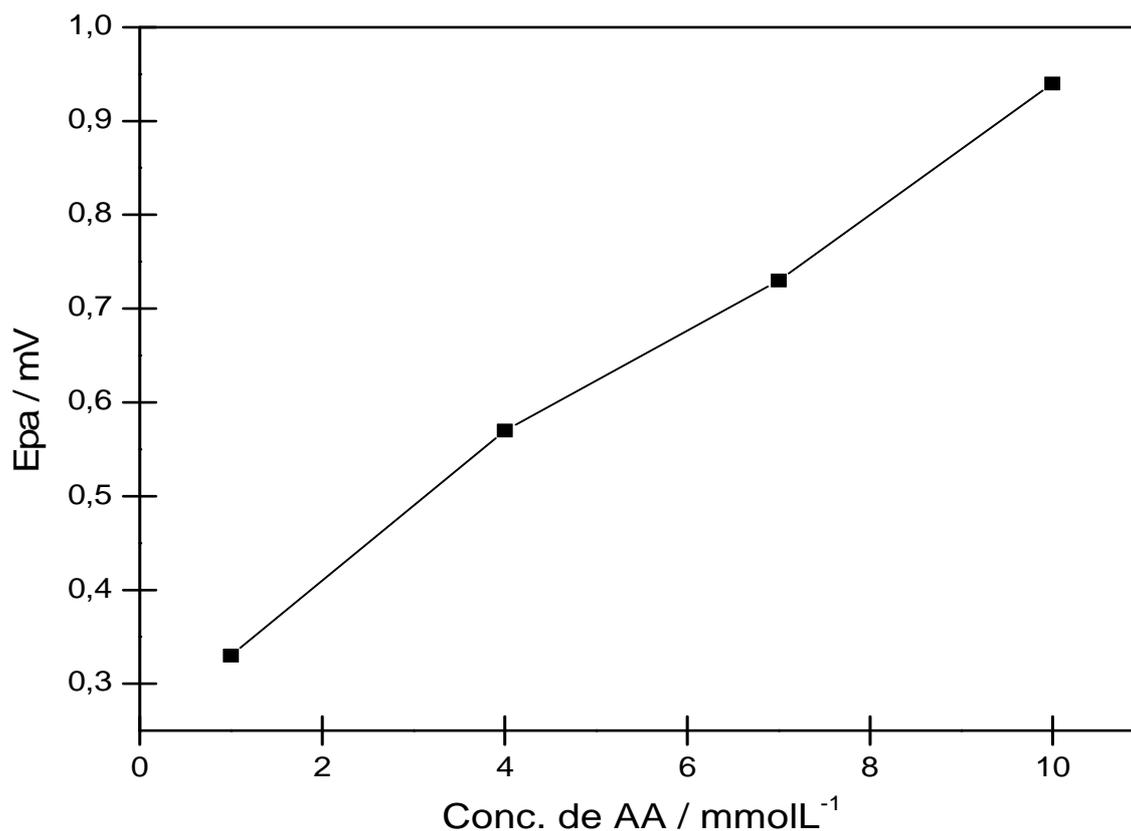


Figure 4: Values of cathodic peak potential taken from the voltammograms shown in Figure 2, as a function of the concentration of ascorbic acid.

3.2 Effect of scan rate

It can be observed that the current anodic peak increases as the scan rate increases, and it shifts to the right, that is, to a region of more positive potential. The values of current peak and the peak potential were taken from the voltammograms, traced as a function of the scan rate, and are represented in figure 5. As can be observed, the current of anodic peak increases linearly with the scan rate, and there is a change in inclination at 60 mV/s.

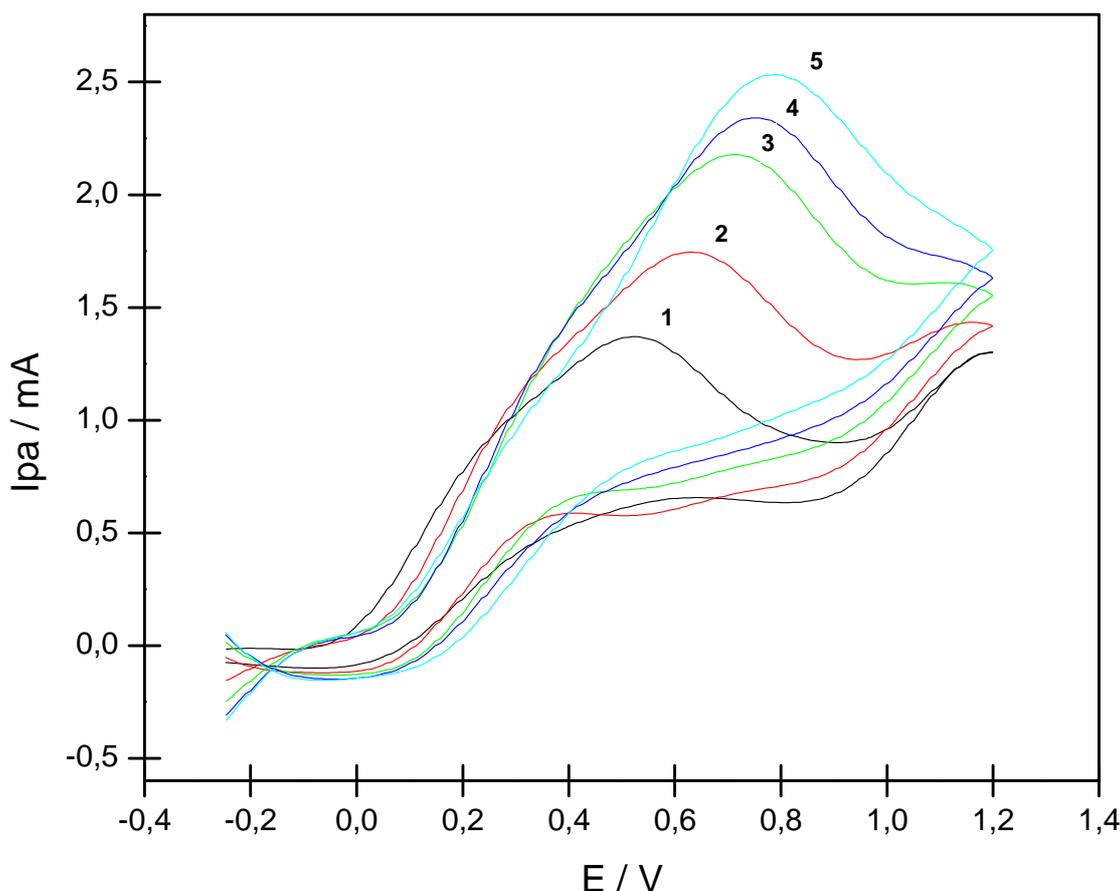


Figure 5: Voltammograms obtained from the modified electrode in a buffer solution with pH= 6, varying scan rate. Curve 1, 20 mVs^{-1} ; Curve 2, 40 mVs^{-1} ; Curve 3, 60 mVs^{-1} ; Curve 4, 80 mVs^{-1} ; Curve 5, 100 mVs^{-1} . Concentration of ascorbic acid, 10 mmolL^{-1} , ambient temperature.

The linear increase of the anodic peak current (Figure 6) with the increase of the scan rate indicates that the transference of charge between the species within the polymeric film takes place more rapidly, and the change of inclination in the curve above 60 mVs^{-1} means that the mechanism of the redox process is different for high scan rates. According to the literature, the linear increase of the anodic peak current with the square root of the scan rate indicates that mass transport is controlled by diffusion (HU et al 2006, ZHANG et al 2007). SHARP et al (1979) proposed a mathematical model that shows that the anodic peak current is proportional to the concentration of electro-active species on the surface of the electrode.

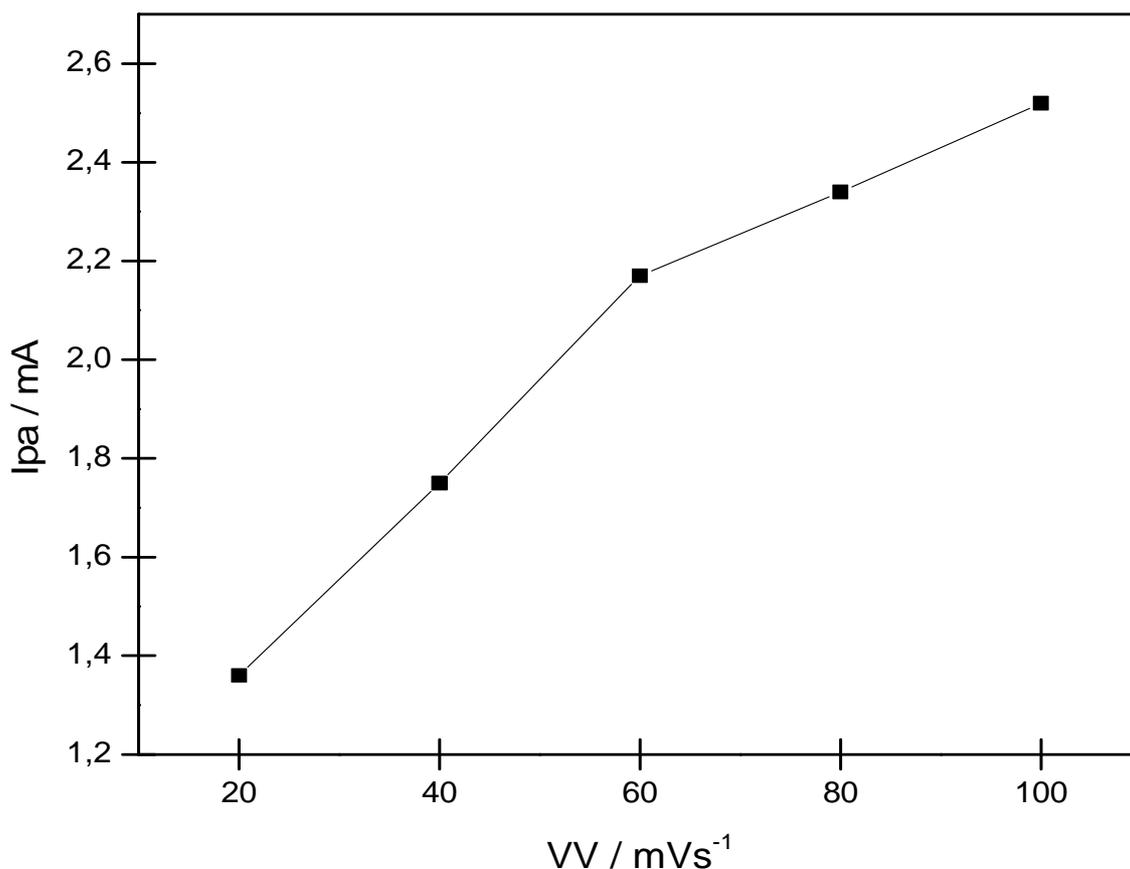


Figure 6: Values of anodic peak current, taken from the voltammograms shown in Figure 5, as a function of the scan rate. Concentration of ascorbic acid, 10 mmolL^{-1} , ambient temperature.

HU et al. (2006) also investigated the effect of scan rate on the parameters of the peaks of the voltammograms obtained from the oxidation of ascorbic acid using a modified electrode; a composite of polyaniline/polysulfone on the platinum surface. The authors suggested that the linear increase in the peak of anodic current is proportional to the square root of the scan rate and the concentration of the electro-active species in the solution. The shift of the potential to more positive has a more exponential behavior, i.e., the values tend to maximum. This indicates that there is a limitation to the diffusion process, that is, at very high scan rates the concentration of ascorbic acid on the surface of the electrode does not vary. According to the literature (HU et al, 2006) there is a kinetic limitation in the reaction of ascorbic acid with the modified electrode.

3.3 Effect of solution pH

The effect of the pH on the electro-catalytic oxidation of the ascorbic acid using the platinum electrode with poly-3-methylthiophene is represented in Figures 7, 8 and 9. As can be observed, the anodic current peak is relatively small and does not vary in case of pH values below 4. In pH values above 4 the current peak increases, considerably and linearly, as the pH of the solution increases.

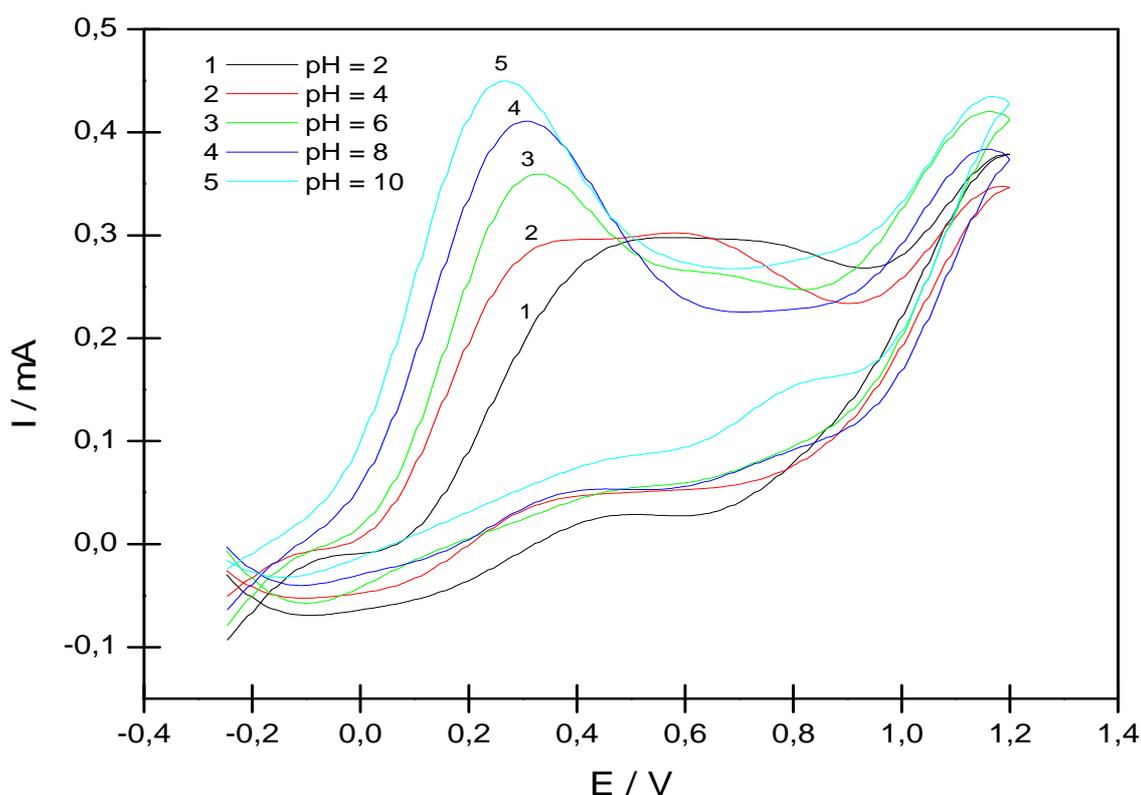


Figure 7: Voltammograms obtained from the modified electrode, varying the pH of the buffer solution. Curve 1, pH = 2; Curve 2, pH = 4; Curve 3, pH = 6; Curve 4, pH = 8; Curve 5, pH = 10. Scan rate, 50mVs^{-1} , concentration of ascorbic acid, 10 mmolL^{-1} , ambient temperature. The film was grown in a 0.1 solution of lithium perchlorate in acetonitrile containing 0.1 molL^{-1} of monomer.

According to the literature (ARANHA et al, 2000), the pKa of ascorbic acid is around 4.17. At a pH any lower than this, ascorbic acid molecules remain in their neutral form, i.e. the protons are linked to the oxygen atoms; at higher pH values, the molecules lose protons and gain a negative charge. As the surface of the modified electrode is charged positively due to the oxidation of the polymeric film, the ascorbate anions are electrostatically attracted to the surface of the electrode, where oxidation takes place by means of the transfer of electrons between the species. Thus, the linear increase of the anodic peak current as pH increases may be related to a higher concentration of ascorbate ions at a higher pH.

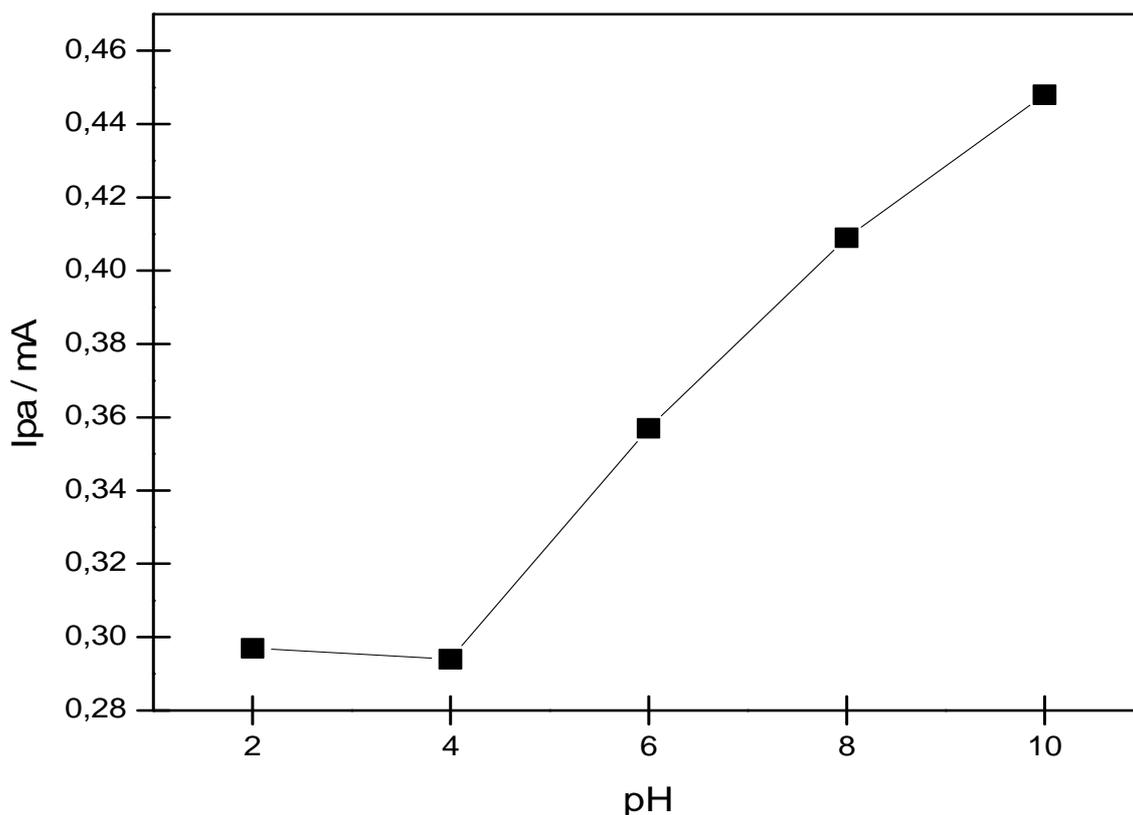


Figure 8: Current values of anodic peak, taken from the voltammograms shown in figure 7, according to the pH of the solution. Concentration of ascorbic acid: 10 mmolL^{-1} ; room temperature.

Figure 9 shows that the potential of anodic peak diminishes exponentially as pH increases. This shift of the potential towards more negative values indicates a favoring of the oxidation process of ascorbic acid as pH increases. The behavior of the curve shows that there are limitations to the kinetic process of charge and mass transference. The electro-chemical oxidation reaction of acid ascorbic involves the loss of two protons and two electrons (KURIHARA et al, 2004). It is therefore expected that in a more alkaline environment the loss of protons is favored and, consequently, so is the loss of electrons. This limitation shown by the change in the inclination of the curve may be associated with the degradation of the polymeric film in a highly alkaline means.

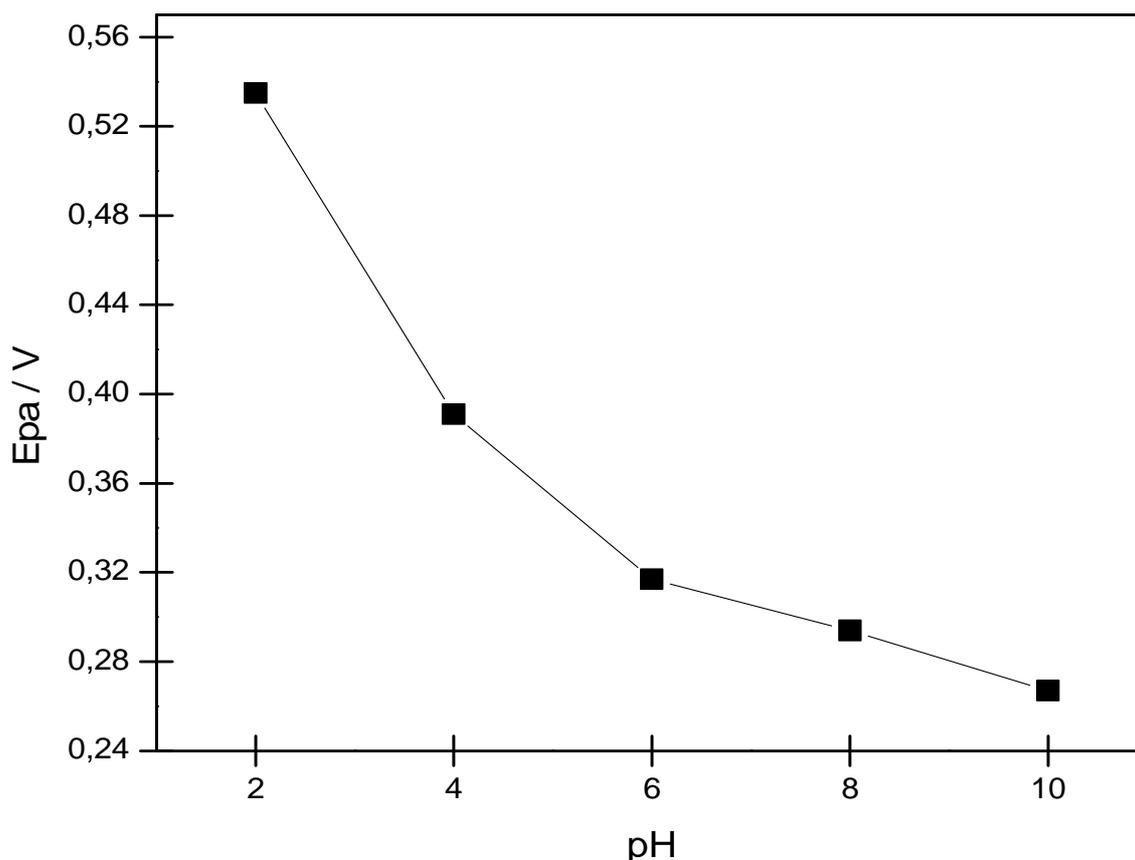


Figure 9: Values of anodic peak potential, taken from the voltammograms shown in figure 9, according to the pH of the solution. Concentration of ascorbic acid: 10 mmolL^{-1} ; room temperature.

4. CONCLUSION

According to the results, we can conclude that the platinum electrode containing the film of poly-3-methylthiophene, modified electrode, presents electro-catalytic activity and good selectivity for ascorbic acid. This electrode can therefore be improved and used as a sensor for the identification of ascorbic acid in natural systems.

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