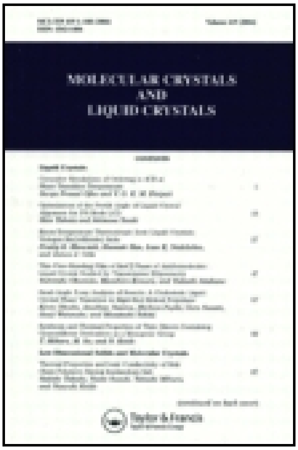

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Electropolymerization Studies of PAni/(poly)luminol Over Platinum Electrodes

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Electropolymerization Studies of PAni/(poly)luminol Over Platinum Electrodes

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This work presents a cyclic voltammetry study of the polyaniline/polyluminol copolymer on platinum electrodes. The results show that under determined conditions it is possible to obtain the copolymer deposited on a metallic surface. The luminol presence clearly affects the oxidation of aniline in the nucleation process and, additionally, changes the cyclic voltammetric characteristics of the obtained material. In this aspect, the copolymer presents hybrid characteristics when compared to the polyaniline and polyluminol separately obtained and seems to present intermediary conductivity.

Keywords: copolymerization; cyclic voltammetry; luminol; PAni; polyaniline; polyluminol

1. INTRODUCTION

The interest in conjugated polymeric materials with electroluminescent properties is related to different branches of technological applications [1,2], as the development of organic light emitting diodes (OLED) [3], solar cells [4] and modification of electrode surfaces for electroanalysis [5,6], electrocatalysis [7–9] and photoelectrochemistry [10,11], as examples. This interest is mainly related to the physical stability and flexibility of such materials, as to the relatively simple methods of

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[*] Actual address: Combustion and Propulsion Laboratory, National Institute for Space Research, Rod. Presidente Dutra, km 40, Cachoeira Paulista – SP, 1263-000. E-mail: eveline@lcp.inpe.br

Address correspondence to Artur J. Motheo, Laboratory of Interfacial Electrochemistry – Institute of Chemistry of São Carlos, University of São Paulo, Av. Trabalhador São Carlense, 400 – C.P. 780, São Carlos, 13560-970 SP, Brazil. E-mail: artur@iqsc.usp.br fabrication. In this aspect, the use of electro polymerized luminol (polyluminol), in the development of surface modified electrodes has been considered [7,9,12,13], due to its strong chemiluminescent character and high luminescent efficiency.

Electropolymerization methods are commonly used to obtain and study a variety of conjugated polymers films deposited over electrodes. The most common examples are the polyaniline (PAni) [14–17] and the polypirrole [18–20]. Under determined conditions, the application of the technique results in the formation of mechanical stable films over electrodes surfaces and, consequently, is ideal for the fabrication of modified electrodes for the most different applications.

In the case of luminol electropolymerization, detailed information on polyluminol (PLum) electro polymerization on platinum, in acidic media, was reported by Zhang *et al.* [12]. The results had shown that PLum can be electro polymerized over platinum electrodes at a constant potential, 1.2 V versus saturated calomel electrode (SCE), or by cycling the potential between −0.2 and 1.2 V (SCE), resulting in a conjugated polymer with a polymerization mechanism similar to that of (PAni). The resultant material has shown good stability in acidic media and was used as a flavin electroluminescent sensor with good sensibility and selectivity.

Another positive aspect in using electropolymerization to obtain PLum is related to the low solubility of luminol in aqueous solutions. If electropolymerization is used, it is possible to work with low luminol concentrations in solution [12,21], which enables the work in aqueous solutions. Meanwhile chemical polymerization needs larger luminol concentration in solution and should be carried out in organic solvents [22].

Considering these aspects, the aim of this work is to present a cyclic voltammetry study on the electropolymerization of a copolymer, composed by aniline and luminol monomers, from aqueous acid media on platinum electrodes. The results showed here shall point out to the formation of the copolymer instead of to the formation of a mixture composed by two different polymers, resulting in a material of mixed electrical properties.

2. EXPERIMENTAL

All the electrochemical experiments were performed in a single compartment electrochemical cell, using a saturated calomel electrode (SCE) as reference electrode and platinum sheets (0.5 cm^{-2} of geometric area) as working and counter electrodes. The experiments were performed using an AUTOLAB PGSTAT20 (Echo Chemie) potentiostat.

The reagents used in the working solutions were aniline (Aldrich, A. C. S. reagent), luminol (3-amino-phthalhydrazide – Acros Organics) and sulfuric acid (Synth). Aniline was previously distilled under vacuum at 155°C. All the working solutions were made by using MilliQ-UV water.

The electropolymerization processes were carried out in an 1 mol dm^{-3} sulfuric acid solution and different concentration of one or both monomers following two different procedures: i) constant luminol (1 mmol dm^{-3}) concentration and different aniline concentrations (1, 5, 10 and 50 mmol dm^{-3}); ii) different aniline:luminol monomer ratios (10:0, 7.5:2.5, 5:5, 2.5:7.5 and 0:10 mmol dm^{-3}), in order to verify the effect of the luminol presence in the film characteristics. Electropolymerization of PAni in a range of concentrations (1, 5, 10, 50 and 100) and PLum (1 and 10 mmol dm^{-3}) were also performed to verify the monomer and polymer behavior and the best conditions for copolymerization.

The polymeric films were obtained by using CV at a sweep rate of 100 mV s^{-1}, for the desired number of cycles. The electropolymerization process were composed of two distinct steps: nucleation step: potential cycling between -0.15 and 1.2 V by 5 cycles, followed by the cut off of the positive potential limit to 0.95 V, for the polymer growth.

All the experiments were performed at 25 ± 1°C.

3. RESULTS AND DISCUSSIONS

Due to the experimental conditions necessary for the copolymerization studies, it is suitable to understand the PAni electropolymerization behavior in low aniline concentrations, which shows characteristic features, as demonstrated in details by Yang and Bard [15]. Therefore, these characteristics will be briefly discussed here for PAni and PLum films.

The 50th cycle of PAni electropolymerization over platinum electrode for different aniline concentrations can be observed in Figure 1.

As shown in Figure 1a, no polymerization is observed for aniline concentration of 1 mmol dm^{-3}. Low aniline concentrations are favorable to the formation of the dimmer p-aminodiphenylamine (ADPA), due to the decrease of the monomer/radical cation ratio [23]. Therefore, the redox couple A/A', observed at approximately 0.45 V, is associated to the dimmer oxidation. When electropolymerization takes place at the electrode surface, this peak is commonly refereed as degradation peak.

For concentrations equal and higher than 5 mmol dm^{-3}, the PAni electropolymerization takes place at the platinum electrode, due the augment of the monomer/radical cation ratio. In the case of the 5 mmol dm^{-3} aniline concentration (Fig. 1b), beside the couple A/A′,

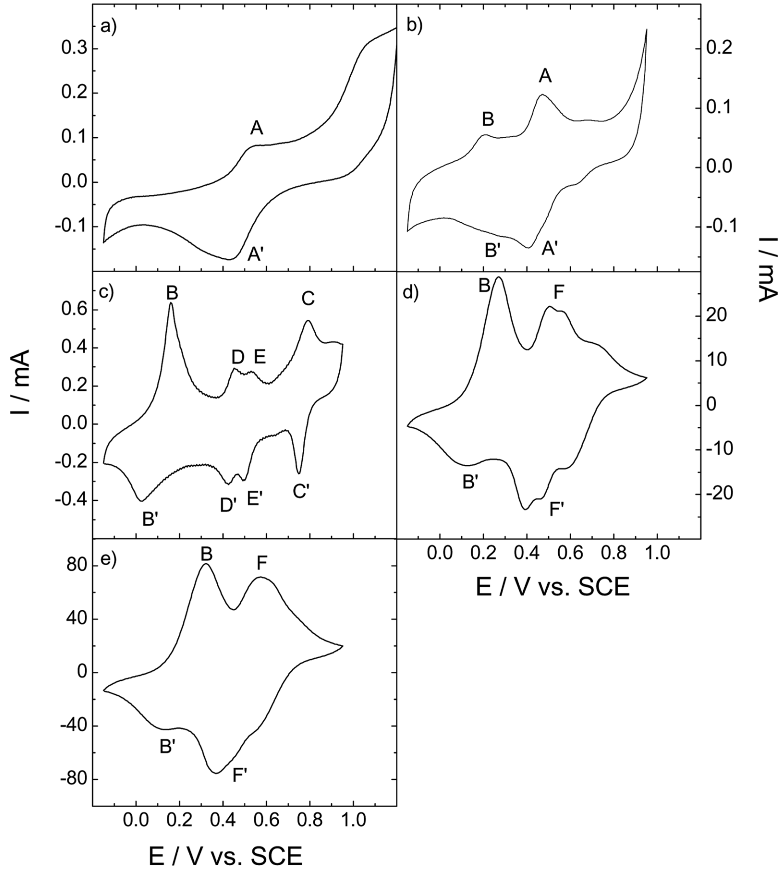

FIGURE 1 Cyclic voltammograms (50th cycle) of the PAni electropolymerization on platinum in H_2SO_4 1 mol dm^{-3} for different aniline concentration. a) 1, b) 5, c) 10, d) 50 and e) 100 mmol dm^{-3}.

mentioned above, two small peaks associated to the polaron redox couple (B/B′) are observed at c.a. 0.2 V, been characteristic of the PAni film. For 10 mmol dm^{-3} aniline concentration Figure(1c), the two peak couples mentioned above are accompanied by a third couple of peaks (C/C′), at c.a. 0.75 V, related to the bipolaron redox couple. The couples D/D′ and E/E′ are related to the by-products of the PAni super oxidation, as demonstrates by Yang and Bard [15], and are strongly influenced by the anodic switch potential of the cyclic voltammogram.

For aniline concentrations of 50 and 100 mmol dm^{-3}, (Figs. 1d and 1e respectively) the cyclic voltammograms obtained with anodic switch potential over 0.8 V present a significant augment in all the peaks couples observed in the case of Figure 1c. Additionally, there is a coupling between peaks related to the by-products of PAni oxidation and the bipolaron redox couple, in the region F/F′. These features are related to a long aniline oxidation time, due to the anodic switch potential, which takes to a high cation radical concentration in the vicinities of the electrode. In this situation the hydrolysis product formation takes place at the interface.

In the case of luminol, the 10th and 50th cycles of PLum electropolymerization on platinum electrodes can be observed in Figures 2a and 2b, for 1 and 10 mmol dm^{-3}, respectively. Both figures present a redox couple (B/B′), at c.a. 0.5 V (approximately the same potential region where the A/A′ redox couple occurs in the case of PAni polymerizations, as observed in Fig. 1), that increases during the potential cycling. The behavior of the observed redox couple is typical for electropolymerization process and is related to the PLum growth onto the electrode surface.

Additionally, the augment rate of the current density of the B/B′ redox couple indicates a slow growth kinetics when compared to PAni electropolymerization.

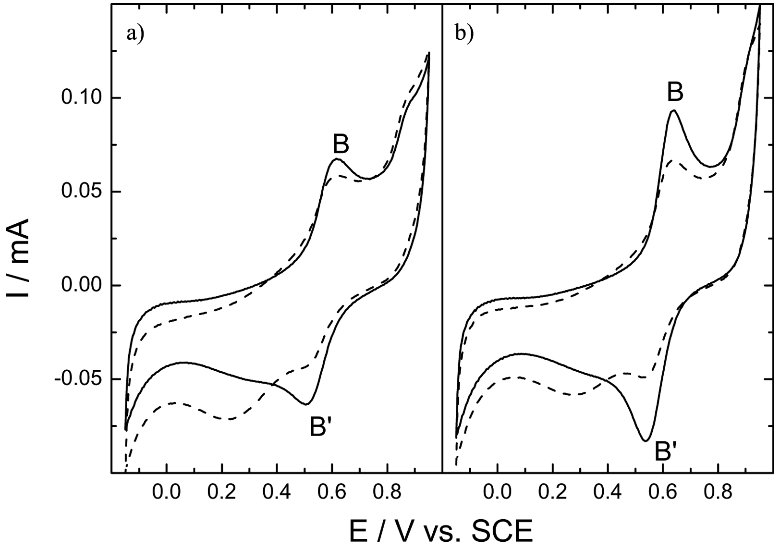

FIGURE 2 Cyclic voltammograms (50th cycle) of the PLum electropolymerization on platinum in H_2SO_4 1 mol dm^{-3} for different luminol concentration. a) 1 and b) 10 mmol dm^{-3}. 10th cycle (- - -) and 50th cycle (—).

The similar electrochemical characteristics of PAni and PLum electropolymerization processes strongly indicate the possibility of copolymerization of the aniline and luminol monomers, to obtain a PAni/PLum film at the electrode surface. However, because of the differences in the kinetics of both independent processes, the monomer ratio between aniline and luminol in the working solution should remarkably influence the copolymerization and must be exploited.

To first understand the monomer concentration influence, we studied the copolymer formation by keeping luminol concentration constant at 1 mmol dm^{-3} in different aniline concentrations. The first cycle of oxidation and nucleation, for film formation, for the different aniline concentration is showed in Figure 3.

In Figure 3a, where both monomers concentrations are the same, the CV shows an addictive character. Two peaks can be observed, the first one at c.a. 0.85 V related to luminol oxidation and the second one at c.a. 0.97 V related to aniline oxidation, as can be seen in the CV's of each monomer (Figs. 1 and 2, respectively).

In Figures 3b–3d, the influence of the aniline concentration in the CV's can be observed, when it increases from 5 to 50 mmol dm^{-3}. In all cases the CV's of the aniline itself present a significant oxidation current increase and the peak potential shifts slightly towards more positive potentials, when the monomer concentration increases. Additionally, an interesting characteristic appears in the monomer mixtures CV's. The concentration increase is followed by an increase in the monomers oxidation however, the currents are remarkably lower than those observed for aniline alone. This feature suggests that luminol can adsorb at the surface preferably than aniline, taking to some aniline oxidation inhibition.

Figure 4 shows the respective CV's for polymers growth related to the same aniline concentrations in Figure 3. In Figure 4a, related to equal monomers concentration, the polymerization of aniline is not observed, however, we observed that PLum formation takes place at this concentration. The redox couple B/B′, related to PLum formation, presents a potential shift towards more positive values of c.a. 5 mV than for aniline, however, the current peak intensity decreases c.a. 20 μA with the luminol presence. At this concentration, it is difficult to affirm that a conductive film was obtained.

When the aniline concentration is increased from 1 to 5 mmol dm^{-3}, the couple B/B′, easily observed in Figure 1b, is not observed in Figure 4b. In this figure the couple shifts towards a potential approximately 50 mV more positive than the observed for couple A/A′ in Figure 1b, with a peak current approximately 40 μA smaller. These features indicate that the incorporation of luminol in the film

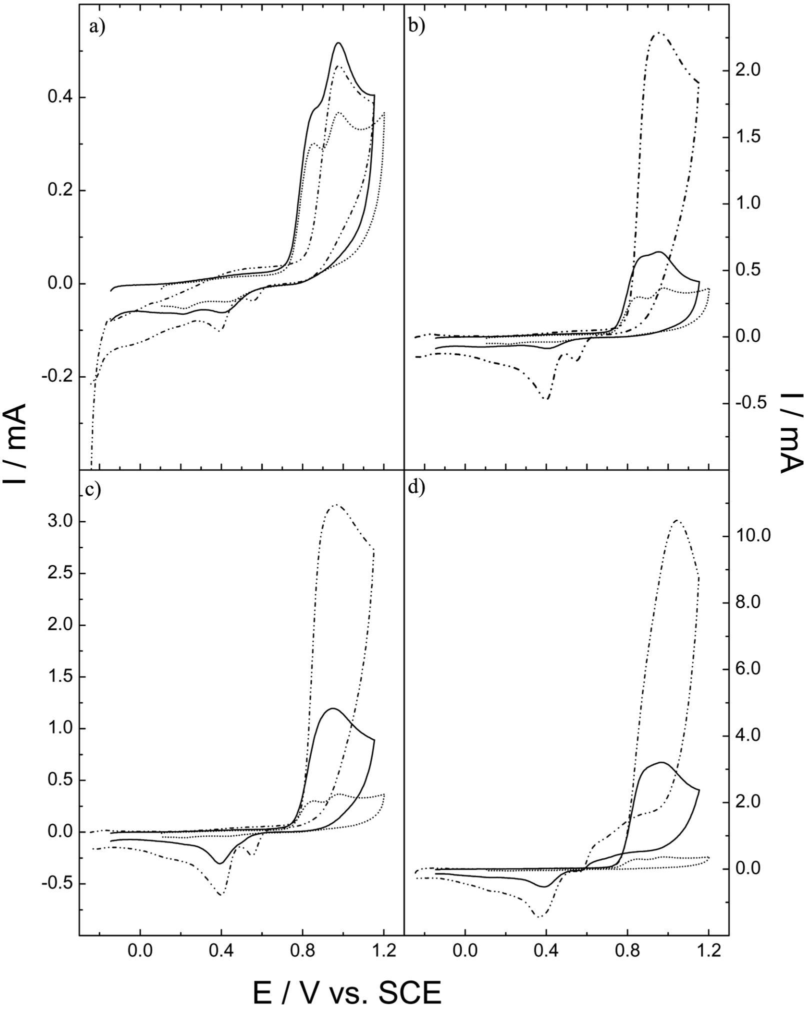

FIGURE 3 Cyclic voltammograms (1st cycle) of monomer oxidation/nucleation on platinum in H_2SO_4 1 mol dm^{-3} and monomer mixtures composed of constant luminol concentration (1 mmol dm^{-3}) and different aniline concentration. a) 1, b) 5, c) 10 and d) 50 mmol dm^{-3} of aniline. (- - -) pure luminol, (·-·-·-·) pure aniline and (—) monomer mixture.

decreases the film conductivity even in small concentrations (5 times smaller) and inhibits the polaron formation.

When aniline concentration is 10 mmol dm^{-3}, the luminol presence causes a remarkable change in the CV profile (Fig. 4c). When comparing

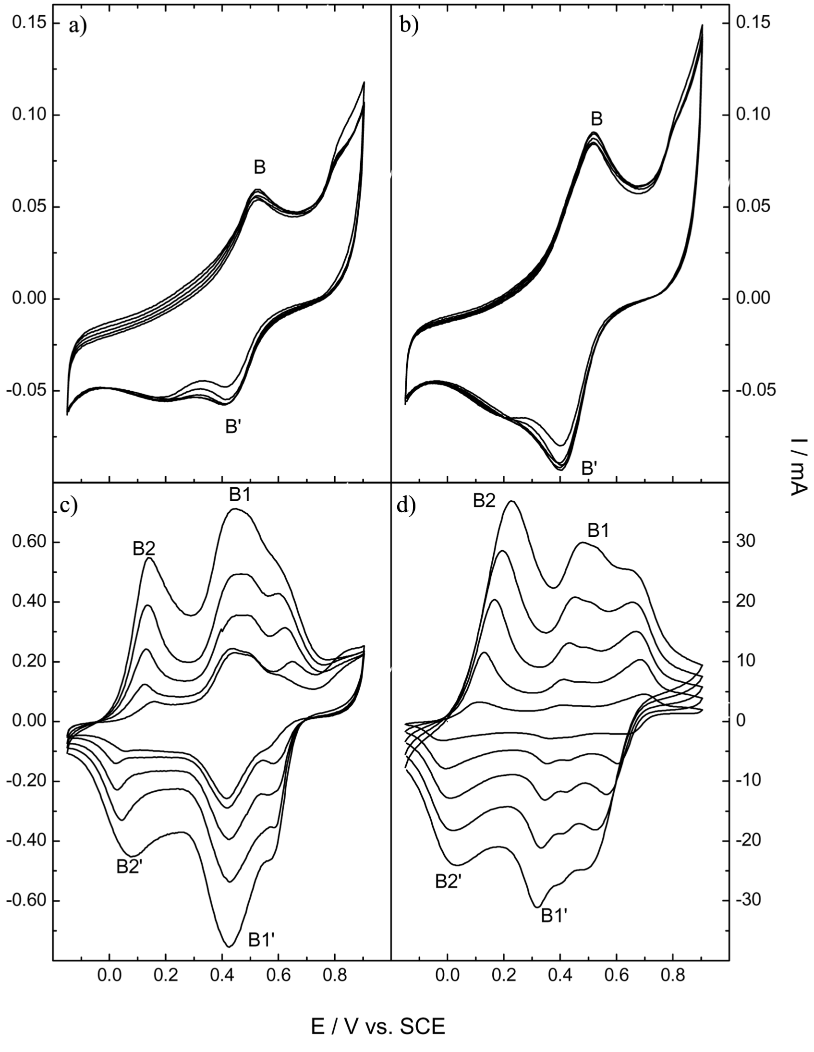

FIGURE 4 Cyclic voltammograms of the PAni/PLum electropolymerization on platinum in H_2SO_4 1 mol dm^{-3} for constant luminol concentration (1 mmol dm^{-3}) and different aniline concentration. a) 1, b) 5, c) 10, d) 50 and e) 100 mmol dm^{-3}.

the CV showed in Figure 1c with that in Figure 4c, in the potential region between c.a. 0.4 V and 0.9 V, the three peaks in Figure 1c merge to the large band observed in the 50th cycle in Figure 4c. This observation leads to two hypothesis; one: the luminol presence increases the hydrolysis product or two: the luminol is incorporated to the polymer film. As the same way than before the presence of luminol causes a decrease in the polaron redox couple current of c.a. 90 μA.

When aniline concentration is increased five times (Fig. 4d), peak B2 at the 50th cycle had an increase of c.a. 8 mA when compared with PAni alone (Fig. 1d). It can be also observed one shoulder at c.a. 0.66 V. In a general way the presence of luminol increases the film currents and the comments made before are also valid.

Another way to verify the influence of luminol presence during the polymer synthesis is changing the monomers ratios. In this aspect Figure 5 shows the CV's for the PLum and PAni electropolymerization and Figure 6 shows those for the copolymer electropolymerization. In these cases the number of growing cycles was increased and the anodic switch potential was changed from 0.950 to 0.8 V in order to avoid the formation of hydrolysis products.

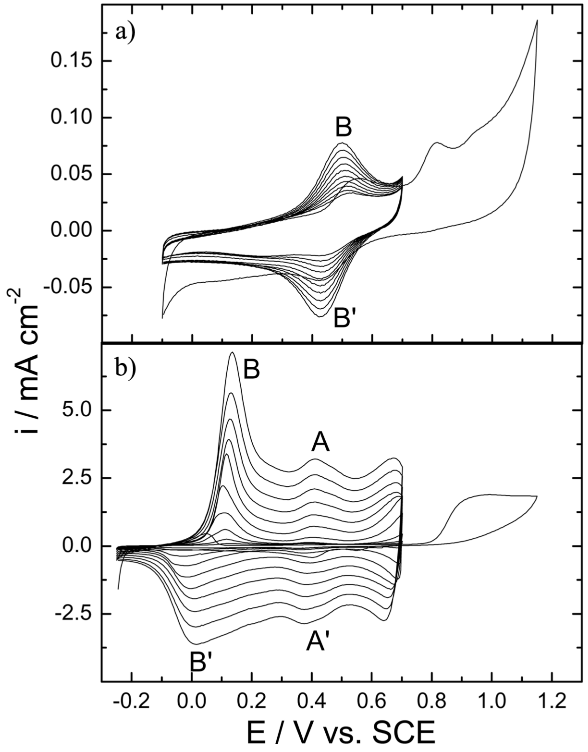

FIGURE 5 Cyclic voltammograms of the PAni and PLum electropolymerization on platinum in H_2SO_4 1 mol dm^{-3} and 10 mmol dm^{-3} monomer concentration. a) PLum and b) PAni.

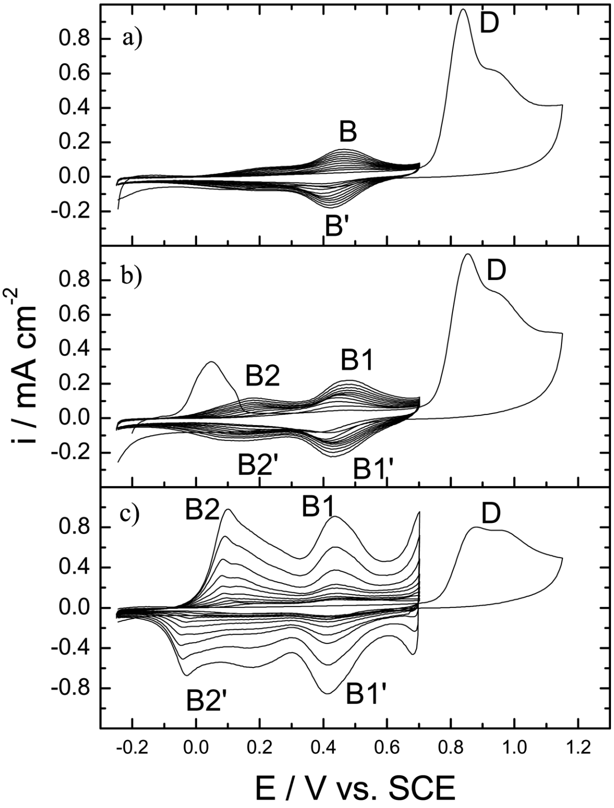

FIGURE 6 Cyclic voltammograms of the PAni/PLum, electropolymerization on platinum in H_2SO_4 1 mol dm^{-3} for different luminol:aniline monomer ratios a) 7.5:2.5, b) 5.0:5.0 and c) 2.5:7.5 mmol dm^{-3}.

A PLum film was obtained with a monomer concentration of 10 mmol dm^{-3} (Fig. 5a). The luminol redox couple B/B′ occurs c.a. 0.500 (oxidation) and 0.422 V (reduction), respectively. As can be seen in Figure 5b, the PAni formation presents two pairs of peaks, B2/B2′ and B1/B1′, the first pair is related to the polaron redox couple and the second pair is related to the hydrolysis products formation, as well known [15].

The CV's in Figure 6 show the mixtures of monomers. The first cycle is related to the oxidation/nucleation step, peak D is associated manly to the luminol oxidation, as stated before, luminol seems to adsorb preferably to the surface, however, the presence of aniline causes a potential shift to more positive values and as the aniline concentration increases the peak current decreases. The existence of a shoulder in c.a. 0.946 V which shifts to more positive potentials and increases the current with the aniline concentration, can be related to its presence.

The oxidation currents of the mixtures lies in a range between 0.8 to 1 mA (peak D), while for the monomers alone is c.a. 12 times lower for luminol and c.a. two times higher for aniline.

The CV in Figure 6a, shows the mixture luminol:aniline concentration 7.5:2.5 mmol dm^{-3}. Peak B presents a shift to more negative potential when compared with PLum alone and the current in the 500th increase c.a. 2 times. The redox couple related to the polaron band of PAni is hardly identified.

When the ratio of monomers concentration is 1:1 (Fig. 6b), the polaron redox couple can be identified (B2/B2′), however its current is lower than the one observed for the redox couple B1/B1′ and is shifted to potentials more positive (0.189 V) than the potential observed for PAni alone (0.136 V). The increase in the current of the 500th cycle for peak B1 when compared with peak B in Figure 6a is c.a. 1.4 times.

From those observations is reasonable conclude that the presence of luminol in ratios of 50% or less leads to a polymer which characteristics resembles more a PLum film than a PAni film.

Above this ratio the film commences to look like more a PAni film as can be seen in Figure 6c, however the polaron redox couple B2/B2′ presents currents very similar than those observed for the couple B1/B1′. Once the process was made in order to avoid the hydrolysis products, from this point we can affirm that the couple B1/B1′ is related to the incorporation of luminol in the polymeric chain.

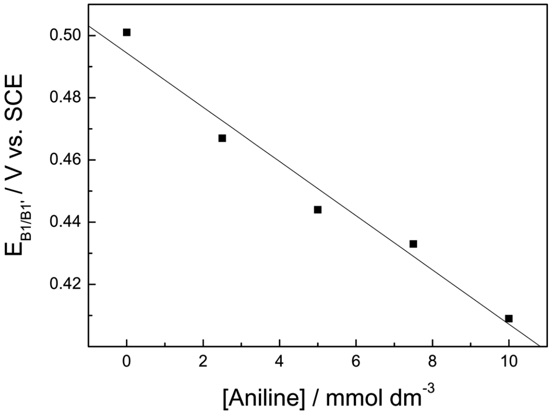

FIGURE 7 Dependence of the peak couple B1/B1′ on the potential for different aniline concentrations in the working solution.

To confirm this statement, the relation between the potential shift of the peak couple B1/B1′ and aniline monomer concentration is shown in Figure 7. It can be clearly observed that the potential of this peak is linear dependent on the monomer concentration, being more influenced by luminol in lower aniline concentration.

4. CONCLUSIONS

The analysis of the cyclic voltammetry studies on the PAni/PLum electropolymerization on platinum enables to draw some conclusions about the formation and properties of the copolymer.

Concerning to the monomers oxidation, the presence of luminol on the solution affects the nucleation step of the polymerization reaction, partially disabling the aniline oxidation due to the possible preferential adsorption of luminol on the electrode surface. Therefore, the concentration ratio between both monomers is determinant to obtain the copolymer. As a consequence, in conditions where the copolymer is electrodeposited, the electropolymerization velocity is limited by the presence of luminol, indicating that it is determinant on the film formation mechanism.

Finally, the obtained PAni/PLum film displays hybrid electrical properties, been lees conductive than pure PAni and presenting a characteristic voltammetric behaviour. Studies on the structure characterization and luminescent properties of the material are in progress.

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