On the pH dependence of electroactivity of poly(methylene blue) films

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ABSTRACT

The electrochemical behavior of poly(methylene blue) on different electrodes has been investigated by electrochemical quartz crystal microbalance and in situ spectrophotometric measurements coupled to cyclic voltammetry. Polymeric films were obtained potentiodynamically and the charge transport mechanism was analyzed. The electrochemical results show that polymer electroactivity depends not only on pH but also on the substrate. Charge compensation changes with both pH and the size of the anions showing a transition in the pH range of polymer pKa. It was demonstrated by spectroelectrochemical experiments that the electroactivity of the film depends on the radical/radical cation equilibrium. The potentials where the most electroactive species are formed have been determined.

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1. Introduction

Methylene blue (MB) chemically modified electrodes (CMEs) offer well recognized advantages in electroanalysis, especially in situations where the target analyte requires high overpotential [1,2]. In general, the characteristics of chemically modified electrodes arises from the advantageous combination of conventional electrochemical techniques with the chemical, structural and other specific properties of the modifying layer(s) [3,4]. Basically, the electrode surface modification can improve the electrochemical signal by mediating or catalyzing the charge transfer reaction [5], protecting the surface against passivation [6] and/or changing the course of the electrochemical mechanism [7,8]. Such electrodes are prepared by immobilizing the chemical species, whose electrochemical properties are known (from solution phase), and thus, they can be used for a very specific application [9]. Most of the immobilized species are able to mediate the electron transfer processes and are used to build electrochemical sensors [10].

Electropolymerization is a powerful tool to prepare CME; electropolymerized materials possess some unique properties that the corresponding monomers not always display and can be immobilized on electrode surfaces. In the past few years, much work has been carried out on electrosynthetised polymers due to their practical application in the construction of sensing surfaces [11–19]. In particular, surface-modified electrodes based on the electropolymerization of several phenazines, phenoxazine and phenothiazine derivatives have been reported in the literature [20,21].

MB is a water-soluble cationic dye molecule that has been widely studied since its synthesis in 1876. It has been extensively used to modified different electrodes surfaces and as effective electron redox mediator [1,2–20,21]. Particularly, was extensively used as mediator in a NAD dependent dehydrogenase biosensor [22,23] and a sensor for hemoglobin based on poly(methylene blue) (PMB) electrodeposited on glassy carbon has also been reported [24,25]. Some studies have shown that when various phenoxazine and phenothiazine-type mediators are immobilized onto zirconium phosphate [2], or incorporated into modernite type zeolites [1], their redox potential values remain constant with pH. Modified electrodes prepared with MB entrapped in a sol–gel ceramic film have been investigated by Khoo and Chen [26] as an electrocatalytic system for the simultaneous identification of ascorbic acid (AA) and uric acid in real samples. A novel composite electrode involving the immobilization of MB on a phosphorylated zirconia–silica matrix, mixed with graphite powder and pressed into a disk format with a strong catalytic activity and well-separated voltammetric peaks for the oxidation of ascorbic acid, dopamine and uric acid has been reported [21]. The use of PMB composite films has been previously explored by Yogeswaran and Chen [27] for qualitative and quantitative simultaneous determination of AA, epinephrine and dopamine in pH = 7.4 aqueous solutions.

The electrochemical behavior of MB at different electrodes have been widely studied [28–30] and it was observed that, as the electron transfer processes occurring at the interface are very fast, only one cathodic peak and one anodic peak are observed in the voltammograms. An interesting feature of the MB electrochemical behavior is that it can form a surface film (equivalent to ca. 60 monolayers) on the electrode surface when it is reduced to Leuco-MB [31]. This film presents conductive properties that are still not

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well understood. Svetlicic et al. [32] and Zutic and co-workers [33] studied the formation of the film using electrochemical methods. These authors have proposed a reduction mechanism for the MB$^+$ in which a mixed valence salt of the radical cation (HMB$^{+\bullet}$) and LMB is formed, which may participate in the conductive mechanism of the film. Several techniques such as optical [34–37], spectroscopic [38–40], electrochemical [20] and electrogravimetric [41–43] have been used to investigate the electropolymerization process of MB or similar molecules.

The aim of this work is to present the spectroelectrochemical and electrogravimetric characterization of the electroactive PMB prepared from the corresponding phenothiazine dye. The electrochemical behavior was investigated by cyclic voltammetry and either in situ UV–vis spectroscopy or piezoelectric microgravimetry with the use of an electrochemical quartz crystal microbalance in different electrolytes; the effect of pH on the reactivity of the films was also investigated. It was demonstrated by spectroelectrochemical experiments that the electroactivity of the film depends on the radical/radical cation equilibrium and the potentials where the most electroactive species are formed, was determined. This is relevant for the use of this kind of modified electrodes as sensors for different analytes where the maximum response must be searched for reliable quantification.

2. Experimental

2.1. Reagents and solutions

The dye methylene blue (Aldrich) was used as received. All solutions were prepared from analytical grade reagents and purified water (UHQ, Elga System).

2.2. Spectroelectrochemical measurements and UV–vis spectroscopy

Spectroelectrochemical experiments were performed under potentiodynamic conditions using a potentiostat/galvanostat Autolab PGSTAT30 (Ecochemie) by placing the electrochemical cell in the optical pathway of a digital fiber optic wheel spectrophotometer (WPIs). After deposition, films were carefully rinsed with purified water and placed in a one-compartment electrochemical cell. A platinum wire was used as the counter electrode and all the potentials are referred to the saturated Ag/AgCl electrode. ITO substrates with sheet resistance ≤20 Ω/cm from Delta Technologies were used and cleaned by using acetone in an ultrasonic bath for 10 min before use.

"*In situ*" UV–vis spectra were recorded in a Hewlett Packard model 8453 spectrophotometer coupled to an EG&G PAR (model 362) potentiostat using a glass cuvette (1 cm path length) as spectroelectrochemical cell. The ITO electrode covered with a methylene blue film was placed in the optical path of the spectrophotometer. For spectroelectrochemical experiments, electrodes were prepared by electrochemical polymerization in 5×10^{-4} mol L^{-1} dye in 0.05 mol L^{-1} phosphate buffer solution (pH = 7) at 0.1 V s^{-1} in the −0.60 to 1.10 V potential range.

2.3. EQCM measurements

Working electrodes for EQCM were AT-cut 6 MHz quartz crystals of 26 mm diameter (Valpey–Fischer). Both sides of quartz crystals were coated with thin (ca. 200 nm thickness) gold films over a ca. 5 nm Cr adhesion layer, but only one of the faces (working electrode) was exposed to the electrolytic solution (active area 0.32 cm^{-2}). A platinum wire was used as counter electrode and all potentials are referred to the Ag/AgCl electrode.

The oscillator circuit ensures oscillation in the series resonant mode as that described in [44]. Electrochemical experiments were carried out with an Omnimetra potentiostat/galvanostat model PG 3901 instrument. Frequency shifts during the potential scans were measured by using a Stanford Research Systems Model SR620 instrument connected to an oscillating circuit (serial mode) and to a microcomputer for data acquisition.

The Sauerbrey equation, $\Delta f = -K \Delta m$ [45], was used to relate the mass changes per unit area, Δm (in g cm^{-2}), to the resonance frequency shift, Δf (in Hz). A K value of 6.45×10^7 Hz g^{-1} cm^{-2} was used for this EQCM, and it was determined by calibration of the device by using the silver deposition method as described elsewhere [46].

After polymerization, films were carefully rinsed with purified water and placed in an electrochemical cell with a free monomer electrolytic solution (KCl or KClO$_4$).

Mass changes obtained from frequency changes can be affected by the non-rigid character of the film, ionic exchange or the swelling effect during electrochemical reactions, which would not allow the direct use of Sauerbrey equation to transform frequency shift in mass. However, this error depends on the film thickness, being negligible for thin films. In this work, it is difficult to obtain a good estimation of the thickness of the film but, studies of conducting polymers films by EQCM it is considered that viscoelastic effects will be minimal for films of about 25 μg cm^2 [42,47]. In our work, films thickness is about 30 μg cm^2, so films are thin enough to consider that frequency variations are mainly due to mass effects.

3. Results and discussion

3.1. Film growth

Fig. 1 shows PMB growth in 0.05 mol L^{-1} phosphate buffer at pH = 7 electrolytic solution with 0.5 mmol L^{-1} dye concentration, under potentiodynamic conditions. As it can be seen in Fig. 1a, three successive redox transitions appear in the potential range studied (regions I, II and III). At potentials more positive than 0.85 V (region I), the current density increase can be associated to radical cations formation, and a continuous current decrease with cycling is obtained. At ca. 0.3 V (region II), current density increases as the polymer is build up on the electrode surface. To neutralize the net charge coming from the oxidation process, anion insertion and cations expulsion occur, causing a global mass increase. This process is reversible; anions are extracted from and cations are inserted into the film on the reduction process, thus causing no net mass change. At ca. −0.08 V (region III) a current density peak is observed, which can be assigned to monomer oxidation [48], and continuously decreases during cycling. The irreversible reaction of radical cation formation together with their combination to form oligomeric species, which can precipitate on the electrode surface, lead to the growth of the polymeric film, and it, is responsible for the progressive mass gain along the voltammetric cycles, as can be seen in Fig. 1b.

Fig. 2a shows both the net charge and mass gain (Fig. 2b) as a function of time during the electropolymerization of MB when the electrode is polarized by a potentiodynamic program between −0.6 and 1.1 V at 0.1 V s^{-1}. Reversible charge and mass changes produced by redox processes in the film are greater as the electropolymerization time increased. It must be pointed out that the ionic exchange during oxidation/reduction became more relevant when the thickness of the film increases. A very important feature to be observed in Fig. 2a and b is that the rate of film formation diminishes as the electropolymerization time increases in agreement with the fact that the oxidation current associated with the radical cation formation also diminishes with cycling. This clearly indicates that
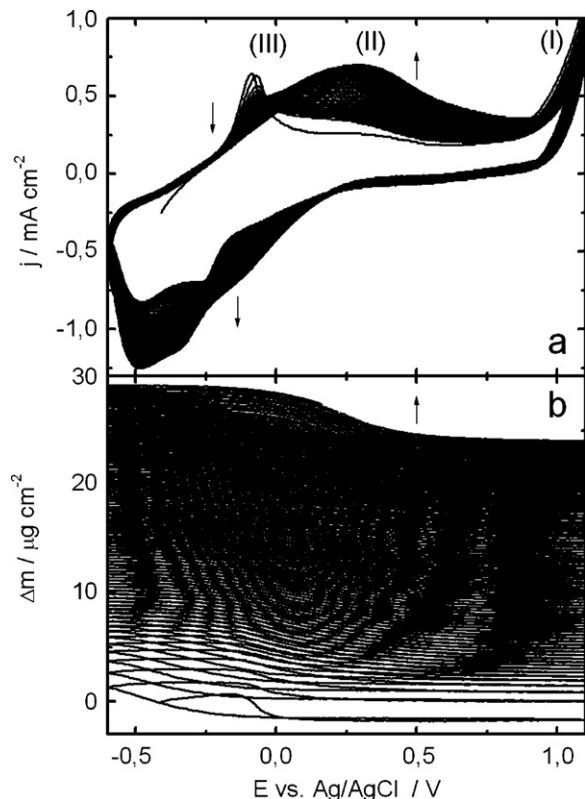
Fig. 1. Electropolymerization j/E (a) and $\Delta m/E$ (b) profiles obtained during poly(methylene blue) formation in a $0.05\,\text{mol}\,\text{L}^{-1}$ phosphate buffer at pH = 7 electrolytic solution with $0.5\,\text{mmol}\,\text{L}^{-1}$ dye concentration. $v = 0.1\,\text{V}\,\text{s}^{-1}$.

the polymer film formed presents some passivating character that could be associated with the film resistance increase or the incomplete achievement of the counterions exchange. Fig. 2c shows the mass/charge plot where a straightforward relationship is obtained with a slope of $0.7\,\text{mg}\,\text{C}^{-1}$. This value is very low as it would indicate that approximately four electrons should be needed per monomeric unit. This would be very unusual considering that other electropolymerization process for aniline or pyrrole, for example, are normally one or two electrons by monomeric unit [49,50]. This clearly indicates that the electrodeposition efficiency is lower than 100% and could be explained taking into account that soluble low molar mass oligomers formation takes place which do not precipitate onto the electrode surface.

3.2. Spectroelectrochemistry and UV–vis in situ

UV–vis spectra of PMB electrochemically deposited onto ITO electrodes at different pH values in $0.1\,\text{mol}\,\text{L}^{-1}$ KCl were obtained at open circuit potential (OCP) and they are shown in Fig. 3. As it can be observed, only one broad band centered in ca. 660 nm with a shoulder at ca. 640 nm, is obtained at all pH values. The absorbance remains practically constant up to pH = 2 and then increases in magnitude for higher pH values. However, the bands wavelengths do not depend on pH. The dependence of the absorbance at 660 nm (A_{660}) with pH is shown in Fig. 4. As already mentioned, this value remains practically constant for low and high pH values, with a transition behavior in the 2.5–8 pH range. OCP of modified ITO electrodes was measured at each pH and is also shown in Fig. 4. A potential diminution with pH up to pH = 8 can be observed, where it remains practically constant. This behavior agrees with already reported results [35] for MB adsorbed onto graphite electrodes where the pKa was determined as being 4.4, in the same region of the transition observed in Fig. 4.
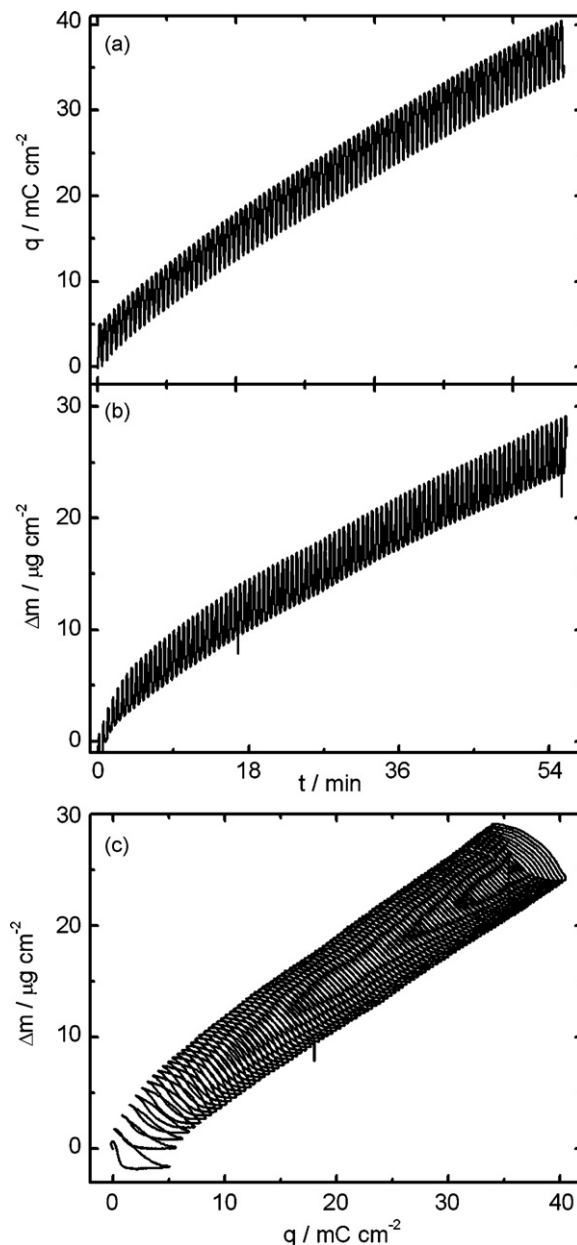

Fig. 2. Charge/t (a), $\Delta m/t$ (b) and $\Delta m/q$ (c) curves obtained during poly(methylene blue) formation in a $0.05\,\text{mol}\,\text{L}^{-1}$ phosphate buffer at pH = 7 electrolytic solution with $0.5\,\text{mmol}\,\text{L}^{-1}$ dye concentration. $v = 0.1\,\text{V}\,\text{s}^{-1}$.

Fig. 5 shows the voltammograms of a PMB together with the absorbance variation at 660 nm and the dA/dt curves calculated from the A/t profiles in $0.1\,\text{mol}\,\text{L}^{-1}$ KCl solution at different pH values. The voltammetric profiles show a quasi reversible process with an anodic and a cathodic peaks; with a potential value that shifts to negative values as the pH increases. On the other hand, it is clearly seen that as proton concentration decreases, the voltammetric peaks become broader and the cathodic peak splits. It is worth noting that the film electroactivity diminishes with pH together with a loss of optical contrast, especially at pH = 8.6 when the electrode does not bleach in the same extent when reduced, as at pH values of 1.54 and 3.5. This must be related to a redox process that is inhibited at higher pH values. As absorbance (or transmittance) is an integral quantity while the current is a differential one it would be better to analyze this relationship by comparing two differential quantities, current and dA/dt [51]. As can be seen in Fig. 5, the redox process associated with chromophore groups absorbing
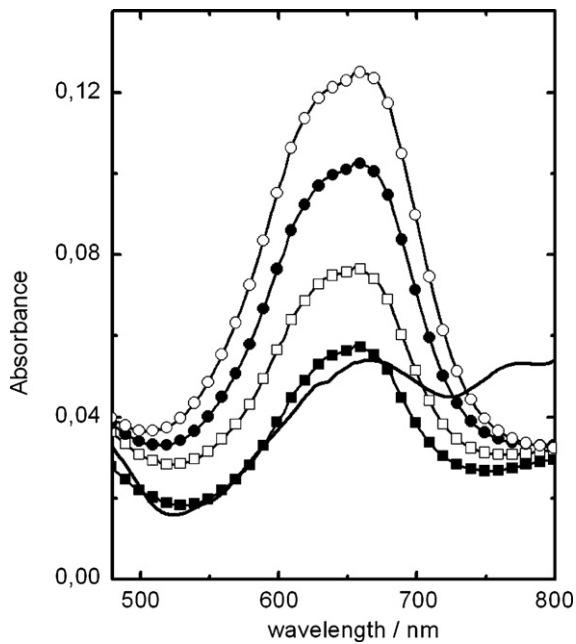
Fig. 3. Visible spectra recorded at OCP condition in different pHs KCl 0.1 mol L^{-1} solutions of poly(methylene blue) films deposited onto ITO electrodes, pH = 0.6 (—), 1.6 (■), 3.6 (□), 5.1 (●) and 8.60 (○).

at 660 nm is that occurring at less positive potentials because dA/dt curve overlaps the first portion of the voltammetric curve. As pH increases, the cathodic peak splits and the dA/dt curve follows the reduction peak taking place at more negative potentials indicating that the species absorbing at 660 nm is reduced at this point.

It was already proposed the reaction mechanism of heterogeneous oxidation of MB [38,39] from a leuco-form (LMB) to MB$^+$ through two successive electron transfers with a fast proton exchange. For polymer deposited on electrodes and by a parallelism with the monomer adsorbed on solid surfaces [35], the oxidation mechanism could be described as follows with the formation of a mixed valence radical cation (HMB$^{\bullet+}$) that is in pH dependent

Fig. 5. j/E (●) A/E (—) and dA/dt (○) potentiodynamic profiles recorded at 660 nm for a poly(methylene blue) film in 0.1 mol L^{-1} KCl electrolytic solution, pH = 1.54 (a), pH = 3.50 (b) and pH = 8.60 (c). $v = 0.05$ V s^{-1}.

equilibrium with the deprotonated radical species.

$$\text{Poly(LMB)} \xrightarrow{-e^-} \text{Poly(HMB}^{\bullet+}) \xrightarrow{-e^-} \text{Poly(MB}^+)$$
$$-\text{H}^+ \downarrow\uparrow +\text{H}^+$$
$$\text{Poly(MB}^{\bullet}) \qquad\qquad (1)$$

Spectroelectrochemical data would indicate that the species absorbing at 660 nm is poly(MB$^{\bullet}$) which is less electroactive than the radical cation for the formation of poly(MB$^+$) and it is related to the redox process taking place at less positive potentials.

3.3. Cyclic voltammetry and EQCM

Fig. 6 shows the steady-state j/E and $\Delta m/E$ potentiodynamic profiles recorded at two different pH values in KCl electrolyte. It can be seen that in both cases the oxidation process goes together
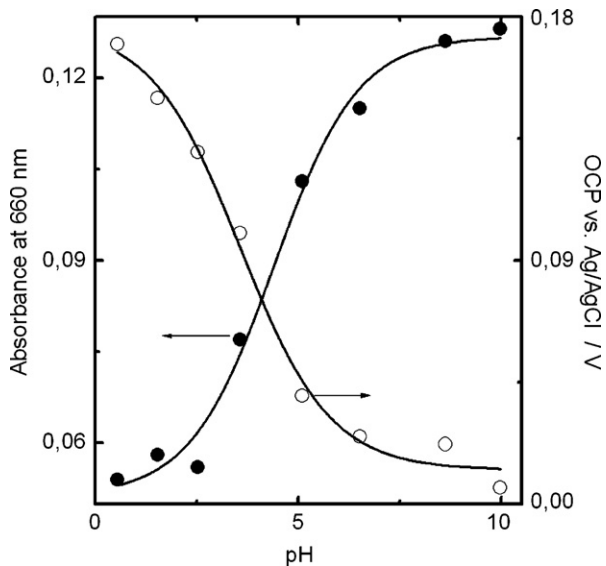

Fig. 4. Dependence of the intensity of the band at 660 nm (A_{660}) and the open circuit potential (OCP) on pH for poly(methylene blue) ITO modified electrode. Data taken from Fig. 3.
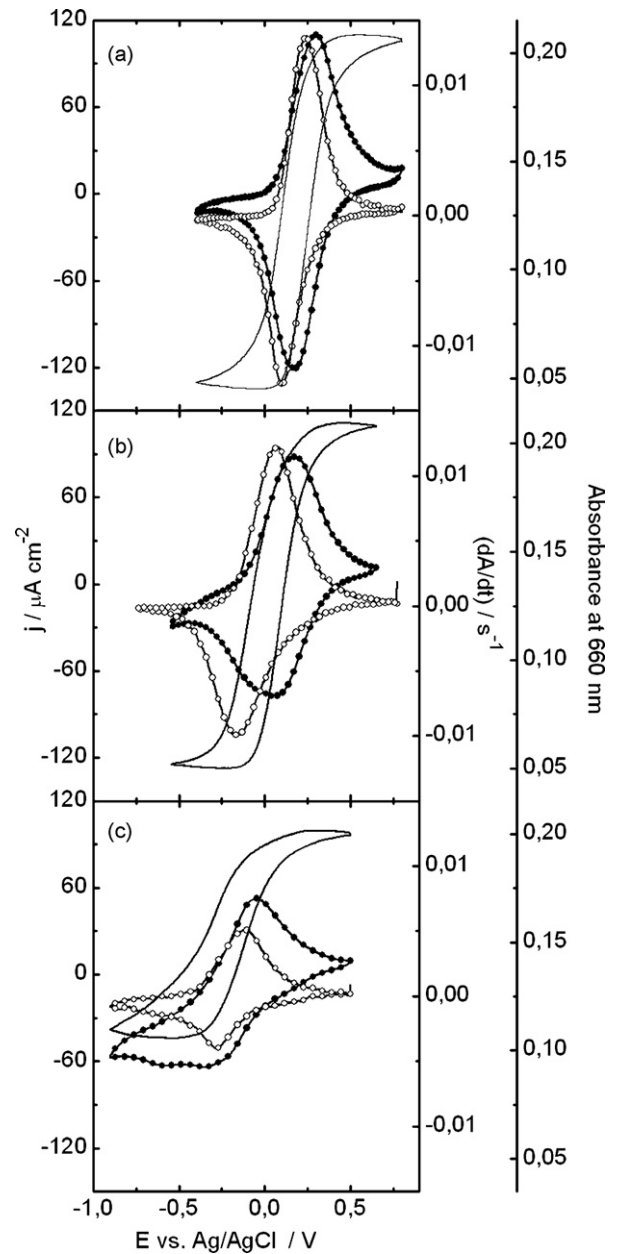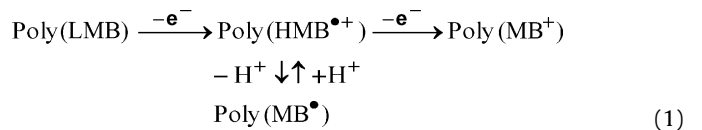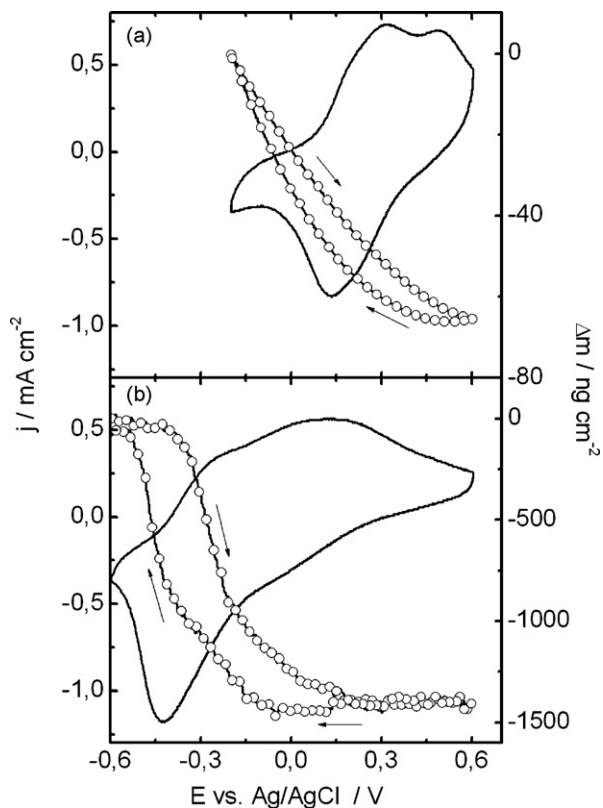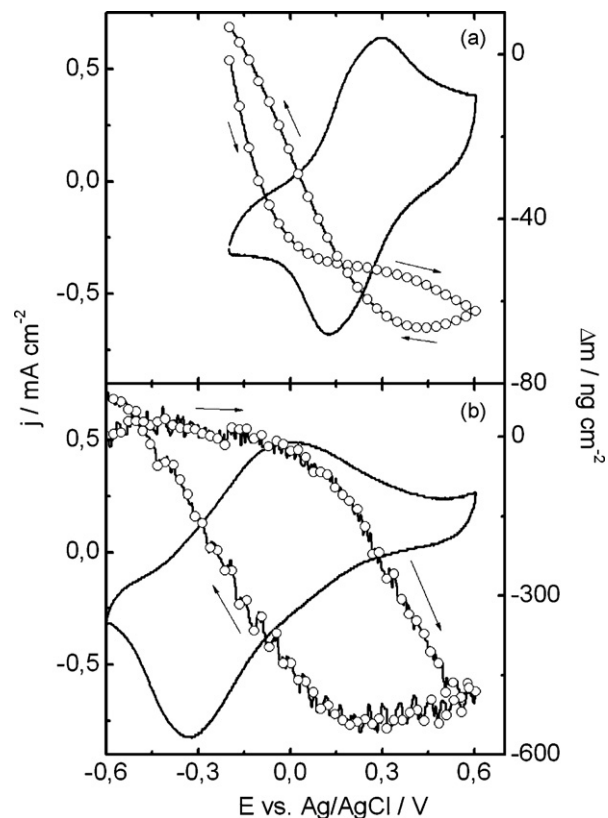
Fig. 6. Potentiodynamic j/E (–) and $\Delta m/E$ (○) profiles for PMB films in 0.1 mol L^{-1} KCl solution at different pH values: (a) 1.54 and (b) 8.60. $v = 0.05\,\mathrm{V\,s^{-1}}$.

Fig. 7. Potentiodynamic j/E (–) and $\Delta m/E$ (○) profiles for PMB films in 0.1 mol L^{-1} KClO$_4$ solution at different pH values: (a) 1.54 and (b) 8.60. $v = 0.05\,\mathrm{V\,s^{-1}}$.

with a mass diminution, being more important at pH = 8. By comparing both Fig. 6a and b, it is clear that, although cations and anions participate in the charge compensations process, cations expulsion during the oxidation becomes more important at pH = 8 than at pH = 1. At this point, it is important to emphasize that the electrochemical response is strongly influenced by the substrate. By comparing Figs. 5 and 6, the shift to less positive potentials with increasing pH values is observed for both substrates, ITO and Au. However, the electroactivity loss with pH already pointed out for ITO, is not observed with gold substrates. Another striking fact that must be mentioned is that both anodic and cathodic peaks are clearly split in the case of Au substrate, indicating that the separation of the two electronic processes described in the reaction is more evident for these substrates.

The electrolyte composition influence was analyzed by steady-state j/E and $\Delta m/E$ potentiodynamic profiles recorded at two different pH values in KClO$_4$ electrolyte (Fig. 7). By comparing with results shown in Fig. 6, the most striking feature to be noted is the dependence of not only the voltammogram but also the mass profile on the different anions used. While in chloride solutions the charge compensation is performed mainly by the accommodation of cations at higher pH values, in perchlorate electrolyte, the charge compensation is achieved by the participation of both positive and negative ions as it can be inferred by the smaller mass diminution.

To perform a detailed analysis of ions participation in the charge compensation process as a function of pH, the global molar fraction of both Cl$^-$ and ClO$_4{}^-$ in the whole oxidation process, was calculated using the procedure already reported [49,52,53] and it is shown in Fig. 8. As it can be seen, while the participation of chloride ions is strongly dependent on pH, the amount of perchlorate ions exchanged is poorly affected. It is important to point out that the transition of the anion molar fraction occurs at the same pH range of that already mentioned for the intensity of the band at 660 nm
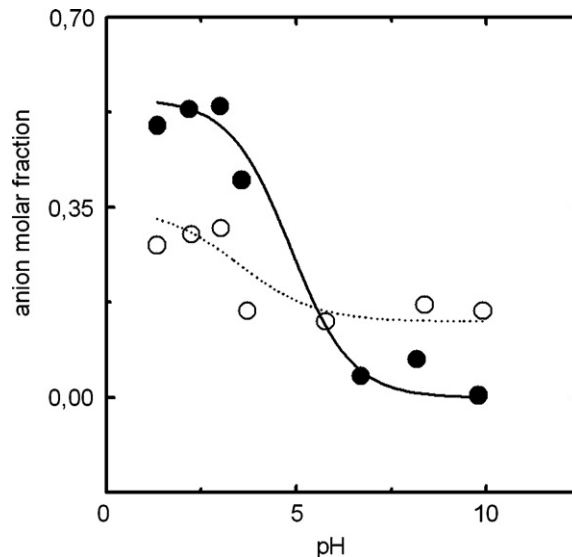

Fig. 8. Plot of the global anionic molar fraction as a function of pH for (●) KCl and (○) KClO$_4$. The lines are only as a guide for eyes indicating a tendency.

(Fig. 4), coinciding with MB pKa value [39]. Obviously, the size of the anion plays an important role as for perchlorate electrolyte both anions and cations participate in a similar way independently on the polymer protonation degree.

4. Conclusions

Electropolymerization of MB in buffer phosphate pH = 7 electrolytes is limited due to the formation of soluble low mass

oligomers leading to deposition efficiency lower than 100%. The spectroelectrochemical response of PMB strongly depends on the electrolyte pH and the association of dA/dt profiles with j/E curves allows to infer that the species absorbing at 660 nm is poly(MB$^\bullet$) which is less electroactive than the radical cation for the formation of poly(MB$^+$) and it is related to the redox process taking place at less positive potentials. EQCM studies show the influence of the polymer protonation degree on the nature of the ions exchanged during the redox process, the participation of anions being more important at low pH values and the size of the anions playing an important role in this exchange.

Acknowledgements

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