Copper dissolution in bromide medium in the absence and presence of hexamethylenetetramine (HMTA)

A.G. Brolo¹, M.L.A. Temperini *, S.M.L. Agostinho

Instituto de Química da Universidade de São Paulo, C.P. 20780, 01498-970 São Paulo, Brazil

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Abstract

The anodic electrochemical behavior of copper in bromide medium, in the absence and presence of hexamethylenetetramine (HMTA), has been studied, using electrochemical and spectroelectrochemical techniques. The copper dissolution in the absence of HMTA was dependent on mass transport of bromide ions. A porous CuBr film was formed at positive overpotentials. The film growth mechanism followed the nucleation, growth and superposition (NGS) model, with instantaneous nucleation and a diffusion-controlled growth of a three-dimensional film. In the presence of the inhibitor, a passivant Cu/HMTA/Br⁻ film was observed. This film has slow growth kinetics, favored by mass transport. The inhibitory effect was observed for the potential range between 0 mV and +800 mV (SCE). A maximum inhibitory efficiency, near 100%, was observed for 15 mM HMTA. The nature of the passivant film was confirmed by in situ surface-enhanced Raman scattering (SERS) and SEM/EDX measurements.

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Keywords: Corrosion inhibitor; Copper corrosion; Hexamethylenetetramine (HMTA); Surface Raman spectroscopy; SERS

1. Introduction

Copper corrosion in different media and conditions has been extensively studied [1]. The role of anions, such as sulfate [2], fluoride [3], chloride [4, 5], bromide [6], thiocyanate [7], carbonate [8] and bicarbonate [9], on the copper anodic dissolution and passivation has received special attention. Recently, the dependence of the mechanism of copper corrosion on the pH has also been reported [10]. It is well established that the copper dissolution process yields either Cu⁺ or Cu²⁺ derivatives, depending on the nature of the electrolyte. For instance, the monovalent cation is stabilized in halide (except F⁻) and pseudohalide media; and Cu²⁺ compounds are more likely to be found for copper corrosion in sulfate and carbonate/bicarbonate media [1].

The mechanism for copper dissolution in bromide medium has been established in a series of papers by Brossard and co-workers [11–14]. In the absence of any CuBr precipitate on the electrode surface, the dissolution occurs according to the following steps:

\[
\text{Cu} + 2\text{Br}^- \rightarrow \text{CuBr}_{2(1)} + e^- \quad \text{1st step}
\]

\[
\text{CuBr}_{2(1)} \rightarrow \text{CuBr}_{2(3)} \quad \text{2nd step.}
\]

Where the subscripts i and s are related to interfacial and solution species, respectively. The diffusion transport of CuBr₂ (2nd step) is the rate determining step in this situation [13]. However, as the anodic current density becomes large enough, CuBr precipitates on the electrode surface.

* Corresponding author. Fax: +55 11 815 5579; e-mail: mlatempe@iq.usp.br

¹ Current address: University of Waterloo, Department of Chemistry, Waterloo, ON, N2L3G1, Canada.
The mechanism for copper dissolution in the presence of CuBr film, showed below, is different, since CuBr reacts with Br⁻ forming soluble complex anions, such as CuBr₂ and CuBr₃⁻ [14].

\[
\text{Cu} + \text{Br}^- \rightleftharpoons \text{CuBr}_{(s)} + e^- \quad \text{1st. step}
\]

\[
\text{Cu} + n\text{Br}^- \rightleftharpoons \text{CuBr}_{(s)}^{1-n} + e^- \quad \text{2nd. step}
\]

\[
\text{CuBr}_{(s)}^{1-n} \rightarrow \text{CuBr}_{(s)}^{3-n} \quad \text{3rd. step}
\]

The diffusion of \( \text{CuBr}_{(s)}^{1-n} \) species into the solution (3rd step) is the rate determining step. The anodic current eventually reaches a limiting value, which is equal to the dissolution rate of the CuBr precipitate accumulate on the electrode surface [14].

The mechanism for copper dissolution in bromide medium is similar to the one in chloride medium [15]. However, the formation of Cu(II) have been reported for copper dissolution in chloride medium [16, 17] at relatively lower overpotentials than for copper dissolution in bromide [12].

Several inhibitors for copper corrosion have been widely studied mainly in those media where the copper dissolution mechanisms are known [18]. Therefore, various works can be found describing the action of inhibitors for copper in Cl⁻ [19–22] and SO₄²⁻ [23–25] media. However, despite the mechanism for copper dissolution in bromide medium has been determined, it is still difficult to find studies about the action of corrosion inhibitors in this medium [26].

In a previous work, we reported the effects of hexamethylenetetramine (HMTA) as an inhibitor for copper dissolution in bromide medium [27]. We showed that HMTA is an effective corrosion inhibitor for copper in bromide medium containing either Fe(III) or O₂ as oxidants. Corrosion potential measurements indicated that the anodic process was not completely diffusion controlled even in the absence of the inhibitor. Potentiostatic and potentiodynamic anodic polarization curves for copper dissolution in bromide solutions containing HMTA were shifted to more negative potentials due to the complexing action of HMTA on Cu(I) ions. The total anodic current became zero at more positive potential values due to the formation of the passivant film. The Tafel analysis showed a decrease in the \( \frac{dE}{d\log I} \) slope as the HMTA concentration increased. The oxidation mechanism was quasi-reversible while the CuBr₂ species were the only oxidation product, and it was not affected by the presence of HMTA. The inhibitory action was observed for [HMTA] ≥ 3.0 mM. The anodic process was not diffusion controlled in the entire polarization curve for these HMTA concentrations. The passive film was characterized by fluorescence spectroscopy as being a Cu(I)/HMTA/Br⁻ complex.

The objectives of this work are to understand some aspects of the mechanism for CuBr and Cu/HMTA/Br⁻ films formation during the copper dissolution process, and further characterize the nature of the passivant film.

2. Experimental

2.1. Electrodes

The working electrode was a 0.50 cm diameter rotating disk electrode built with an electrolytic copper plate (99.9% purity). It was mechanically polished with 300, 400 and 600 mesh wet emery-paper and rinsed with double distilled water, prior to use. A cylindrical polytetrafluoroethylene sleeve was pressure fitted onto the rotating disk electrode. A complete description of the electronic equipment used is given elsewhere [28]. A platinum foil was used as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode.

2.2. Solutions

The electrolyte solutions were prepared from analytical grade reagents and double distilled water. HMTA was reagent grade and it was used without further purification. The pH values of the electrolyte solutions containing HMTA were adjusted to 3.0 with HBr aqueous solution. Bubbling of the solution with N₂ was carried out for 30 min before the measurements, and a weak stream was maintained above the solutions during the experiments. All experiments were performed at \( (25 \pm 1) \)°C.

2.3. Electrochemical instrumentation

The electrochemical system used was a PAR (potentiostat–galvanostat) model 273 coupled to an IBM personal computer which contain the data acquisition and the data treatment software. The curves were recorded on a HP 7090A plotter.

2.4. SEM and EDX instrumentation

Environmental scanning electron microscope model E-3 was used for SEM analysis. The electron gun was operating at 20 kV. The cathode filament current was set to 1.37 A. The instrument is equipped with an Oxford link EDX analyzer model 6380 and silicon detector. In contrast to an older EDX analyzer, this model is supplied with a state of art thin electron win-
2.5. Raman instrumentation

In situ Raman spectra from the copper electrode were obtained with a Renishaw 1000 Raman microscope system equipped with a Peltier-cooled CCD detector and a holographic notch filter. A macropoint accessory, with 40 mm of focal length, was used to redirect the laser light to the electrode surface. The spectroelectrochemical cell has been described elsewhere [29].

A 35 mW Melles Griot He–Ne laser provided excitation at 632.8 nm. The laser power was ca. 6 mW at the sample.

3. Results and discussion

A typical cyclic voltammogram for a stationary Cu electrode immersed in 0.1 M KBr solution, pH = 3.0, is presented in Fig. 1. Two anodic peaks, labeled A1 and A2, and two cathodic peaks, C1 and C2, were observed. According to Brossard [11], the formation of soluble CuBr2 species occurs before the peak A1. The first anodic peak (A1) is due to the formation of a CuBr precipitate on the electrode surface. After this first saturation the electrochemical reaction continues to occur through the porous film and a second anodic peak, labeled A2, is observed (Fig. 1). The CuBr formation is still the predominant process in the A2 region [12]. The cathodic peak C1 is related to the reduction of these surface species. The cathodic peak C2 was not reported before [12].

Figs. 2A and 2B show the voltammograms for the copper dissolution in acidic bromide medium (pH = 3) in the presence of 6.0 and 15.0 mM HMTA (stationary electrode), respectively. For 6 mM HMTA (Fig. 2A), at sweep rate equal to 10 mV/s, the voltammogram was similar to the one obtained without the inhibitor (Fig. 1), except by the presence of an anodic pre-peak, App (identified in Fig. 2A). The App peak was strongly dependent on the HMTA concentration. The current ratio, I_{App}/I_{A1}, was higher for more concentrated HMTA solutions (Fig. 2B). The passivant effect was also more evident for copper dissolution in bromide medium (pH = 3) containing 15 mM of HMTA (Fig. 2B). The cathodic region observed in Fig. 2B presents several peaks indicating the reduction of different kinds of films.
The results observed in Figs. 1 and 2, suggest that the pre-peak, App, corresponds to the Cu(I)/HMTA/Br\(^{-}\) passive layer formation, and the peak A1 corresponds to the CuBr film. The Cu(I)/HMTA/Br\(^{-}\) film is formed at low positive overpotentials [27], and the CuBr film is formed either through the pores of the first film or on surface regions not completely covered by the HMTA-containing film. The increase of the ratio \(I_{\text{App}}/I_{\text{A1}}\) with the increase of the HMTA concentration (Figs. 2A and 2B) agrees with this assignment (more HMTA in solution seems to favor the formation of the species at App).

SEM measurements were performed in order to confirm these voltammetric results. The SEM image, obtained from a Cu electrode submitted to a similar condition as presented in the anodic part of Fig. 2A, showed a film on the electrode surface with few patches. This result indicates that part of the electrode was not covered by the inhibitory film. Elemental chemical analysis on the film and inside the patches were performed. The results are summarized in Table 1. The analysis of the film showed a fair amount of nitrogen, which indicates the presence of HMTA. On the other hand, chemical analysis of the patches showed mainly Cu and Br.

Table 1
<table>
<thead>
<tr>
<th>Region</th>
<th>Nitrogen</th>
<th>Bromine</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>film</td>
<td>0.0691</td>
<td>0.0776</td>
<td>0.8365</td>
</tr>
<tr>
<td>Patches</td>
<td>—</td>
<td>0.0420</td>
<td>0.9333</td>
</tr>
</tbody>
</table>

The observations from Fig. 3 indicate that the copper anodic dissolution products (in 0.1 M bromide medium and pH = 3 in the absence of HMTA) formed in A1 and A2 are reduced in C1 and C2, respectively. This result contradicts a previous work [12] which claims that the species formed in both A1 and A2 are reduced together in the cathodic region C1. However, cathodic potentials studied in Ref. [12] were not negative enough to allow the observation of the peak C2. It seems evident that the peak A1 is related to the formation of CuBr film which was reduced at C1. This hypothesis is in agreement with the experimental data presented here and with other prior works [11–14, 27]. The nature of the peaks A2 and C2 are unclear, and it will be discussed in the following paragraphs.

Following the mechanism for copper oxidation in chloride medium, one can suggest that the anodic peak A2 is due to the formation of Cu(II) ions [16]. Nevertheless, the oxidation of the CuBr film is not the main reaction that occurs at the anodic peak A2. This
conclusion is supported by the following observations: first of all, the anodic peak A2 (at potential more positive than A1, see Fig. 1) was clearly related to the cathodic peak C2 that appears at potentials more negative than C1 (Fig. 3). Therefore, the specie formed in A2 was kinetically more stable than the species formed in A1. Besides, the Cu(II) species are generally more soluble than Cu(I) derivatives, therefore, the peak C2 should decrease when the electrode was rotated (RDE experiments), which was not observed. The Pourbaix diagram for copper in 1 M bromide medium [26] predicts that the formation of Cu(II) starts at potential more positive than +800 mV versus SCE. Finally, the Cu(II) ions are blue in aqueous medium and this color was noticed only when the potential was swept to values more positive than those showed in Figs. 1 and 3.

Another possibility is that the peak A2 is due to a copper oxide formation. Copper oxides are very stable and the film could remain in the surface even at very negative potentials. However, the formation of copper oxides is not expected for copper dissolution in acidic medium free of oxygen. In fact, the equilibrium potential-pH diagram (Pourbaix diagram) for copper in chloride medium shows that, at lower pH, the oxidation of CuCl should lead to the formation of Cu^{2+} ions instead of copper oxides [32]. The same is observed in the Pourbaix diagram for copper in 1 M bromide solution [26].

The mechanism for copper dissolution in bromide medium (presented in Section 1) suggest that CuBr is the predominant species in both regions A1 and A2 [12]. Therefore, there are two possible explanations for the nature of the anodic peak A2 and the cathodic peak C2 (not considering the possibility of Cu(II) and copper oxides formation). First of all, one can consider that a CuBr film (type I) is formed in A1. This type I film must be porous and permits the reaction to continue to occur through the pores, leading to the formation of another kind of CuBr film (type II) with different morphology, which is responsible for the anodic peak A2. The type II film is more stable and it is reduced at potentials more negative than the cathodic peak C1. Another possibility takes into account that A2 is related to the limiting current of the CuBr film dissolution (3rd step in the mechanism for dissolution of a copper electrode covered with CuBr presented in Section 1). In this case, the C2 peak must be connected to the reduction of the species possibly generated during the localized attack of copper.

Fig. 4 presents the voltammograms for the dissolution of a stationary copper electrode in 0.1 M KBr, pH = 3 in the presence of 15 mM HMTA, at several E_r values. One can observe from Fig. 4 that the cathodic region become complex as the E_r values were made more positive than the potential of the anodic peak A1. The complex cathodic region suggest the reduction of mixed films formed in the anodic sweep.

Fig. 5 shows the dependence of the cyclic voltammograms for copper in bromide medium (pH = 3), in the presence of 15 mM HMTA, on the sweep rate. It can be noticed that the inhibitor was more efficient at low sweep rates (1 mV/s). Almost total passivation was observed for the voltammogram at 1 mV/s (the anodic current is close to zero after the anodic peaks, Fig. 5). The ratio of the anodic currents I_{App}/I_{A1} was higher for the voltammogram obtained at 1 mV/s (the anodic current is close to zero after the anodic peaks, Fig. 5). The ratio of the anodic currents I_{App}/I_{A1} decreased as the sweep rate increased. The small value of the ratio, I_{App}/I_{A1}, for high sweep rates, suggest that the specie responsible for the peak App can not be well formed at fast potential scans. The inverse relationship between I_{App}/I_{A1} and the sweep rate indicates a slow kinetics for the formation of the species responsible for the App peak. In fact, a slow formation rate for the Cu(I)/HMTA/Br^- film has been demonstrated in our previous work [27].

Fig. 6 shows the dependence of the cyclic voltammograms of copper in 0.1 M bromide medium (pH = 3) containing 15.0 mM HMTA on the stirring of the solution. As it can be observed in Fig. 6, a more efficient
protective film is formed on the electrode which was rotated at 16 Hz. The results presented in Fig. 6 indicates that the mass transport favors the inhibition process. In the voltammogram under stirring \( f = 16 \) Hz, only one cathodic peak at ca. \(-360\) mV and one anodic peak at ca. \(-104\) mV was observed. Besides, peak A$_1$ did not appear in the voltammogram under stirring. These results suggest that, for the system under stirring, only a compact Cu/HMTA/Br$^-$ film is formed. In contrast, the voltammogram of the non-stirred solution \( f = 0 \) Hz in Fig. 6) presents several cathodic peaks due to the reduction of mixed films, and the anodic current increased as the potential become more positive than \(+100\) mV.

Chronoamperometry can be used for film formation mechanism studies. A theoretical model for multiple nucleation phenomena followed by diffusion controlled growth of three dimensional centers was developed [33]. The nucleation process can either be progressive or instantaneous [33]. This nucleation, growth and superposition (NGS) model has been successfully applied to several systems [34, 35].

Chronoamperograms were obtained by stepping the potential from \(-1.0\) V \( (E_{\text{initial}})\) to different positive potential limits \( (E_{\text{final}})\). Fig. 7 shows the chronoamperograms for copper in 0.1 M bromide medium (pH = 3), in the absence of HMTA, obtained at several \( E_{\text{final}} \) values (the \( E_{\text{final}} \) values are indicated in Fig. 7).

An exponential current decrease until a constant residual value was obtained for low overpotentials \( (E_{\text{final}} = -100\) mV in Fig. 7). This behavior is expected for an oxidation process with soluble products controlled by mass transport [36]. It has been demonstrated that the soluble CuBr$_2$ is the dominant species at this overpotential [11, 12, 27]. When the \( E_{\text{final}} \) values were made more positive than \(+100\) mV, the chronoamperograms presented the characteristic shape expected in a film formation process. For \( E_{\text{final}} > +100\) mV, an increase in the current was observed at the beginning of the chronoamperogram (initial transient). After a time \( t_m \), the current reaches a maximum value originating a current peak \( (I_m)\), from which the current starts to decrease. This kind of result characterizes the classical behavior of a film formation process by NGS mechanism [33].

The chronoamperograms for copper in 0.1 M bromide (pH = 3), in the presence of 15 mM HMTA, are presented in Fig. 8. The chronoamperograms in the presence of HMTA can be divided in two distinct sets. The first set (set I) comprise the chronoamperograms obtained for \( E_{\text{final}} \leq +400\) mV (Fig. 8). These curves presented an initial increase in the current, followed by complete passivation (current drops to zero). On the other hand, a second set of chronoamperograms (set II) was obtained for \( E_{\text{final}} > +400\) mV. In this case, the shape of the chronoamperometric curves are very similar to the ones obtained in Fig. 7 (in the absence of HMTA). All chronoamperograms obtained in the presence of 15 mM HMTA (Fig. 8), presented values for \( I_m \) lower than the one observed in the absence of the inhibitor (Fig. 7). The maximum current peaks were also reached at lower \( t_m \) values in the presence of 15 mM HMTA. The set I-
type chronoamperograms in Fig. 8 (for $E_{\text{final}} \leq +400$ mV) show rapidly decrease in the current to a value practically equal to zero after the $I_m$ peak, indicating that, in the presence of HMTA, the formed film was not porous. This film completely blocked the surface and prevent the copper oxidation reaction. For $E_{\text{final}} \geq +600$ mV (set II curves in Fig. 8), the chronoamperograms were similar to the ones without the inhibitor, suggesting that there was a competition between the formation of CuBr and Cu(I)/HMTA/Br$^-$ films. The porous CuBr film was formed preferentially, even in presence of HMTA, when $E_{\text{final}} \geq +600$ mV, due to the slow kinetics of the Cu/HMTA/Br$^-$ passive film formation. These results are in accordance with those obtained by cyclic voltammetry.

The mechanism for the film formation can be verified by comparing the experimental chronoamperogram with theoretical curves, for progressive and instantaneous nucleation, considering a NGS-type mechanism, using the expressions [33]:

\[
I^2 = \frac{1.9542}{T_m} \left( \frac{t}{t_m} \right)^2 \left[ 1 - \exp \left( -1.2564 \left( \frac{t}{t_m} \right)^2 \right) \right]
\]

for instantaneous nucleation, and

\[
I^2 = \frac{1.2254}{T_m} \left( \frac{t}{t_m} \right)^2 \left[ 1 - \exp \left( -2.3367 \left( \frac{t}{t_m} \right)^2 \right) \right]
\]

for progressive nucleation.

The experimental (from Fig. 7, for copper in 0.1 M bromide, pH = 3, without HMTA) and the theoretical
curves relating to dimensionless parameters \((I/I_m)^2\) and \((t/t_m)^2\) are presented in Fig. 9. Curve A shows the experimental chronoamperogram for the system without inhibitor (from Fig. 7), while curves B and C are the calculated results for instantaneous and progressive nucleation process, respectively. The result in Fig. 9 clearly shows that the CuBr film formation occurs through a NGS mechanism. The nucleation is instantaneous, and the growth is controlled by diffusion. This result agrees with previous work which consider that the film formation is controlled by the mass transfer of bromide ions [11]. The electrocrystalization of other copper dissolution products have also been found to follow the NGS mechanism [37]. The diffusion coefficient of bromide was also determined from the NGS model (see Refs. [34] and [35] as examples of the procedure). The average value for the diffusion coefficient of bromide was ca. \(1.6 \times 10^{-5}\) cm²/s, which was in fair agreement with voltammetric determinations (1.8 \(\times 10^{-5}\) cm²/s in Ref. [11]).

Unfortunately, a similar quantitative treatment was not possible for the chronoamperograms in the presence of HMTA (Fig. 8). Despite the curves showed in Fig. 8 for \(E_{\text{final}} \geq +600\) mV (set II) being very similar to the ones obtained in the absence of inhibitor, a critical analysis of these curves becomes difficult due to the supposedly presence of a second film of CuBr, which competes with the formation of Cu/HMTA/Br⁻. The shape of the chronoamperograms obtained in the presence of HMTA for \(E_{\text{final}} \leq +400\) mV (set I in Fig. 8) does not correspond to the NGS model with diffusion controlled growth. These curves suggest a two dimensional nucleation-superposition process rather than three dimensional. In this case, the Cu/HMTA/Br⁻ nuclei are formed and grow parallel to the surface, forming a compact, non-porous, layer. According to the voltammetric data presented before, the nuclei growth is controlled by diffusion. As the superposition occurs, the surface is completely blocked, leading to immediate decrease in the total current to zero.

Another interesting feature appears when the chronoamperograms in the absence (Fig. 7) and in the presence of HMTA (Fig. 8) are compared at short time intervals. Fig. 10 presents this comparison for \(E_{\text{final}} = +200\) mV. According to Fig. 10, for \(t < 0.05\) s, the anodic current in the presence of the inhibitor was higher than the current obtained in the absence of HMTA. This behavior confirms the complexing effect of HMTA observed before [27], and the low rate for the passive film formation. The current values presented in Fig. 10 are practically constant in both curves for \(t > 0.4\) s.

The electric charges can be extracted from the chronoamperograms, and the efficiency \(\theta\) of the inhibi-
The inhibitor can be calculated using the following expression:

\[ \theta = \frac{Q_0 - Q_{\text{HMTA}}}{Q_0} \]

Where \( Q_0 \) and \( Q_{\text{HMTA}} \) are the electric charges in the absence and presence of HMTA, respectively.

Fig. 11 shows the dependence of the efficiency of the inhibitory action (\( \theta \) values), obtained (by the integration of the chronoamperograms) for 6.0 and 15 mM HMTA, on the final potential (\( E_{\text{final}} \)). A much higher efficiency for more concentrated HMTA solutions (15 mM HMTA) up to +400 mV was observed. For \( E_{\text{final}} \) values more positive than +400 mV the inhibitor efficiency decreases sharply. For HMTA 6.0 mM, the inhibiting efficiency increases with the \( E_{\text{final}} \), and above +400 mV it falls down to approximately zero. These results confirmed the existence of a competition between the CuBr and Cu/HMTA/Br\textsuperscript{−} films at higher overpotentials. The negative \( \theta \) at zero volts for 6.0 mM (Fig. 11) is related to the complexing effect of the inhibitor [27].

More information about the nature of the passivant film was obtained by surface Raman scattering experiments. This technique also provided some insights into the understanding of the copper oxidation in the presence of the inhibitor.

The normal coordination analysis and vibrational assignment for HMTA have been performed [38]. SER spectra of HMTA adsorbed on a silver electrode have also been reported [39]. The in situ surface-enhanced Raman (SER) spectra from a copper electrode immersed in a solution containing 1 mM HMTA (0.1 M KBr, pH = 3) at different potentials (before and after the film formation) are presented in Fig. 12, and

![Fig. 12(a).](image-url)
the vibrational frequencies and assignments are presented on Table 2.

Several striking differences can be observed in the spectra presented in Fig. 12 for different applied potentials. The monoprotonated cation (HMTAH\(^{+}\)) is the predominant species in solution throughout our experiments (pH = 3), considering that HMTA is a moderate base \( (pK_a = 6.2) \). However, at very negative potential \((E = -1.2 \text{ V})\), the SER spectrum closely resembled the one observed for adsorbed HMTA on metallic surface [39], with two strong peaks at 778 and 1048 cm\(^{-1}\). The protonation of one of its nitrogen dramatically decreases the basicity of other nitrogen in the HMTA molecule. Being so, the monoprotonated HMTA can only adsorb to the electrode surface by electrostatic interactions (not by acid–base reaction). The amount of specific adsorbed bromide at 

\(-1.2 \text{ V} \) is expected to be small, which avoids the possibility of an ion-pair interaction. Therefore, the HMTA molecule interacts directly with the electrode surface at this potential. The SER spectrum (Fig. 12b) at 

\(-400 \text{ mV} \) (before the copper oxidation) shows an overall shift and splitting in several peaks. Besides, the 778 and 1048 cm\(^{-1}\)-bands' intensities decreased and new strong bands at 794, 1022 and 1061 cm\(^{-1}\) appeared. A strong ca. 1026 cm\(^{-1}\) band is a fingerprint for the monoprotonated HMTA cation [39]. These spectral changes suggest that, as the potential was made more positive, the amount of specifically adsorbed bromide anions increased, which made the ion-pair interaction between HMTAH\(^{+}\) and Br\(^{-}\) possible. The adsorption of HMTA and HMTAH\(^{+}\) before the copper oxidation are illustrated in Fig. 13.

Fig. 12. Surface-enhanced Raman spectra of a copper electrode immersed in 0.1 M KBr + 1 mM HMTA solution at several potentials. Region 1: from 300 to 1500 cm\(^{-1}\). Region 2: from 2700 to 3100 cm\(^{-1}\). Applied potentials: (a) –1.2 V; (b) –0.4 V; (c) +0.4 V.
Fig. 12c presents the in situ spectrum of the Cu/HMTA/Br\(^-\) film formed at +0.4 V. The splitting of several bands is more evident in this spectrum. HMTA is a cage-like compound with \(T_d\) symmetry. The coordination of one of its nitrogen provoke a decrease in the overall symmetry to \(C_{3v}\). Using the correlation table technique [40], it is possible to predict that the degenerated F1 and F2 modes should split into \(A_2+E\) and \(A_1+E\), respectively. The \(A_2\) modes are Raman inactive under \(C_{3v}\) symmetry. The spectrum presented on Fig. 12c is consistent with a monocoordinated HMTA complex. The bands at 760, 1060, 1066 and 2931 cm\(^{-1}\) are probably from HMTAH\(^+\).

**Table 2**

<table>
<thead>
<tr>
<th>Vibrational frequencies(^a) (in cm(^{-1})) and assignment for HMTA adsorbed on the copper electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E = +1.2) V</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>150 (b, s)</td>
</tr>
<tr>
<td>453 (m)</td>
</tr>
<tr>
<td>514 (m)</td>
</tr>
<tr>
<td>704 (w)</td>
</tr>
<tr>
<td>778 (s)</td>
</tr>
<tr>
<td>797 (m, sh)</td>
</tr>
<tr>
<td>810 (m)</td>
</tr>
<tr>
<td>886 (b, m)</td>
</tr>
<tr>
<td>996 (w)</td>
</tr>
<tr>
<td>1012 (w)</td>
</tr>
<tr>
<td>1048 (vs)</td>
</tr>
<tr>
<td>1061 (s)</td>
</tr>
<tr>
<td>1190 (b, w)</td>
</tr>
<tr>
<td>1205 (b, w)</td>
</tr>
<tr>
<td>1236 (m)</td>
</tr>
<tr>
<td>1327 (w)</td>
</tr>
<tr>
<td>1341 (m)</td>
</tr>
<tr>
<td>1371 (m)</td>
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<tr>
<td>1455 (m)</td>
</tr>
<tr>
<td>1474 (w)</td>
</tr>
<tr>
<td>1571 (w)</td>
</tr>
<tr>
<td>2896 (b, s)</td>
</tr>
<tr>
<td>2907 (sh, s)</td>
</tr>
<tr>
<td>2932 (s)</td>
</tr>
<tr>
<td>2959 (s, sh)</td>
</tr>
<tr>
<td>3000 (s), 3006 (sh, s)</td>
</tr>
</tbody>
</table>

\(^a\) Intensities: v — very; w — weak; m — medium; s — strong; b — broad; sh — shoulder.

\(^b\) Frequencies from solution spectrum presented in Ref. [39].

\(^c\) Frequencies from Ref. [38]. Calculated frequencies (from Ref. [38]) are presented in square brackets. The assignment is presented considering a \(T_d\) symmetry.

**4. Conclusions**

The results presented in this work for the copper oxidation in bromide medium, in the absence of the inhibitor, indicate a diffusion controlled process at low anodic overpotentials, while there is the formation of soluble products. At higher overpotentials, a porous CuBr film is formed. The CuBr is the main product for the copper oxidation in bromide medium for overpotentials as high as +800 mV (versus SCE). Two anodic peaks were observed in the voltammogram, which may correspond to two types of CuBr films with distinct morphology. Evidence from localized dissolution of the CuBr film at potentials more positive than +200 mV was observed by cyclic voltammetry and SEM. The CuBr film formation follows a growth mechanism that corresponds to a NGS model, with an instantaneous nucleation and a diffusion (of bromide ions) controlled growth.

The HMTA inhibits the copper oxidation process in bromide medium through the formation of Cu(I)/HMTA/Br\(^-\) film. This film is formed at anodic potential values more negative than the potentials where the
CuBr film is formed, indicating a complexing effect of HMTA on Cu(I) ions. The inhibitory effect of HMTA on copper dissolution was observed for potential values between 0 and +400 mV for \([\text{HMTA}] = 6 \text{ mM}\) and between 0 and +800 mV for \([\text{HMTA}] = 15 \text{ mM}\). For \([\text{HMTA}] = 15.0 \text{ mM}\), the inhibitory efficiency was near 100% in the potential range between 0 and +400 mV (versus SCE). The passive HMTA film has a slow growth rate when compared to the kinetics of formation of the CuBr film. In fact a competition between both types of film occurs. The mixture of these films on the electrode surface was determined by SEM/EDX measurements. The inhibitory HMTA film formation is also strongly dependent on mass transport. The SERS results showed that a HMTAH\(^+\)–Br\(^-\) ion-pair is specifically adsorbed on the electrode surface prior to the oxidation. Therefore, the deprotonation of the HMTA cation is a mandatory step before the film formation. This deprotonation process may be related to the slow kinetics of formation for the inhibitory film.

Considering that the CuBr\(_2\) formation is the first step for the oxidation, the copper dissolution process in the presence of the inhibitor may follow the steps presented below:

\[
\begin{align*}
\text{Cu} + 2\text{Br}^- & \rightarrow \text{CuBr}_2 + e^- \quad \text{1st. step} \\
\text{HMTAH}^+ & \rightarrow \text{HMTA} + H^+ \quad \text{2nd. step} \\
\text{CuBr}_2 + \text{HMTA} & \rightarrow \text{Cu(HMTA)}\text{Br} + \text{Br}^- \quad \text{3rd. step} \\
\text{Cu} + \text{Br}^- & \rightarrow \text{CuBr} + e^- \quad \text{4th. step}
\end{align*}
\]

For low overpotentials and slow sweep rates, the steps 1, 2 and 3 are important. In this case, the first step seems obvious, because, according to our SERS results, the bromide ions are directed adsorbed to the electrode surface. The equilibrium presented in step 2 is also observed from the SERS experiments. At low overpotentials, and slow sweep rates, the soluble CuBr\(_2\) can either diffuse to the bulk solution or react with HMTA to form a protective film. The fourth step became important at higher overpotentials. In these cases (more anodic potentials or fast sweep rates), the CuBr film formation start to compete with the Cu/ HMTA/Br\(^-\). Evidences for multiple film formation in these situations was observed by cyclic voltammetry, chronoamperometry and SEM/EDX.

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