# Effect of Aromatic Amines on the Diffusion Layer Thickness during the Copper Electrodeposition from Acid Bath

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**Abstract:** In this paper we have shown that some aromatic amines like aniline, benzylamine, *N*-methylaniline, *N*-ethylaniline, *N,N*-dimethylaniline, *N,N*-diethylaniline, *o*-toluidine, *m*-toluidine and *p*-toluidine added in the electrolyte solution influence the copper electrodeposition process by decreasing the diffusion layer thickness. Experimental results have been obtained by linear sweep voltammetry and chronoamperometry. The qualitative results obtained by linear voltammetry show a significant effect of aromatic amines on the cathodic copper electrodeposition. The semi-quantitative results obtained by chronoamperometry have been used to determine the diffusion coefficient of $Cu^{2+}$ ions using the Randles – Sevcik equation. The calculated values of the diffusion layer thickness decrease from 40 $\mu$m in the blank electrolyte solution to 13 $\mu$m in the presence of 1 mL $L^{-1}$ *m*-toluidine.

**Keywords:** copper electrodeposition, diffusion coefficient, diffusion layer thickness, chronoamperometry

## 1. Introduction

Copper electrodeposition from acid solution, in the presence of superficial active substances, such as organic nitrogen compounds and inorganic ions, like chloride ions, was extensively studied in the literature in the past decades [1-5]. In most of these studies it is revealed that such compounds act as inhibitors for the copper electrodeposition process through their adsorption at the metal – electrolyte interface. The presence of the organic additives in the electrolyte solution produces a decrease of the cathodic peak current directly proportional to the concentration of the additives. The overall effect of the organic additives is to inhibit the nucleation process and to shift the reduction peak potential to more negative values [6]. However, the superficial active molecules are not permanently adsorbed on the same cathodic areas; at some point desorption and re-adsorption occur on some other cathodic areas where the interfacial concentration of the cations is reduced [7]. Thus, new crystallization germs can form easily on the free cathodic areas. Many of these substances, depending on the electrolyte acidity or basicity, are able to form oligomers by polymerization, at electrode potentials closed to the copper reduction potential. Therefore, the selection of appropriate additives is very important. Compounds containing $-NH_4^+$ cation can be considered as good inhibitors for copper electrodeposition, especially when they are in complex combination with $Cl^-$ or $SO_4^{2-}$ ions, since they shift the copper reduction potential to more negative values.

The rate determining step at current densities closed to the limiting current density is the mass transport [8, 9] but the copper crystals growth, with a layered structure takes place at lower current densities where the charge transfer across the electric double layer is the rate determining step [10].

Although the organic additives generally adsorb on the copper electrode surface, they may exhibit dissimilar catalytic effects. For example, it has been found that benzylamine has a pronounced catalytic effect on the hydrogen evolution reaction in acid solution [11] but the same compound inhibits the $Cu^{2+}$ reduction process [12,13]. The protonation of the benzylamine molecule in acid solution modifies its electronic structure and thus the dipole moment vector, on whose direction the adsorption takes place [14].

The adsorption of the organic additives is also influenced by the presence of other ions in the electrolyte solution. It has been shown that in the presence of $Cl^-$ ions the organic compounds form an adsorbed monolayer on the copper electrode with the thickness depending on the molecule volume, but in the absence of $Cl^-$ ions only a minimal adsorption was evidenced [15]. Another reason for using $Cl^-$ ions in copper electrodeposition, taking into account that $Cu^{2+}/Cu^+$ is the rate determining step, is the stability of $Cu^+$ species in chloride media ($Cu^{2+}$ in chloride media forms only weak complexes) [16]. When both $Cl^-$ ions and reasonable quantities of amines are present in the electrolyte solution, they act as inhibitors only for the $Cu^{2+}/Cu^+$ electron transfer process while the $Cu^+/Cu^0$ reaction remains unaffected [17].

The rate of copper deposition is influenced by several factors, such as the kinetics of $Cu^{2+}$ ions reduction, the electrochemical behavior of organic compounds at the electrode interface and also how the flow of $Cu^{2+}$ ions reaches the electrode surface [18]. It has been found that the adsorption of organic compounds at the interface leads to a decrease of the $Cu^{2+}$ ions diffusion coefficient and of the mass transport rate [19] although the $Cu^{2+}$ diffusion mechanism remains the same.

The aim of this paper is to study the modification of the diffusion layer thickness during copper electrodeposition in the presence of some aromatic amines.

## 2. Experimental

The electrochemical measurements were carried out with a PAR 2273 potentiostat / galvanostat, equipped with specific modules for each method, i.e., PowerCv for cyclic and linear voltammetry and PowerPulse for chronoamperometry.

Experimental determinations were carried out in a conventional three-electrode one-compartment glass cell, using a working electrode made of copper (99.99% Cu) with a surface of 0.5 cm². Two graphite rods were used as counter electrode, and a silver-silver chloride electrode as reference. To compensate the ohmic drop in the electrolyte solution a Luggin capillary was placed close to the working electrode. The working electrode surface was prepared by grinding with different grain sizes SiC paper followed by polishing with diamond powder (DP-Spray Struers) 1 μm grit.

Aniline (A, for synthesis, $\geq$ 99% GC), benzylamine (BA, for synthesis, $\geq$ 99% GC), *N*-methylaniline (MA, for synthesis $\geq$ 98% GC), *N*-ethylaniline (EA, for synthesis $\geq$ 98% GC) *N,N*-dimethylaniline (DMA, for synthesis $\geq$ 99% GC), *N,N*-diethylaniline (DEA, for synthesis $\geq$ 99% GC), *o*-toluidine (*o*T, for synthesis $\geq$ 99% GC), *m*-toluidine (*m*T, for synthesis $\geq$ 99% GC) and *p*-toluidine (*p*T, for synthesis $\geq$ 99% GC) were purchased form Merck and used as received. Sulfuric acid (Merck, p.a., 95–97%) and copper sulfate pentahydrate (CuSO4·5H₂O, Merck, $\geq$ 98%) were used to prepare the aqueous electrolyte solutions.

All experiments were carried out at 25 ± 0.1°C in unstirred solution.

## 3. Results and Discussion

To obtain information about the influence of aromatic amines, chosen as inhibitors for $Cu^{2+}$ reduction process, steady-state polarization curves on copper electrode were recorded. Fig. 1 shows a set of polarization curves recorded on copper from a common galvanic electrolyte solution, based on copper sulfate (20 g L⁻¹ $Cu^{2+}$), sulfuric acid (1.86 mol L⁻¹) and chloride (50 ppm Cl⁻) [20, 21], and different aromatic amines (1 mL L⁻¹).

As it can be observed, the addition of organic amines generally leads to a decrease of the peak current density compared to the blank electrolyte solution. This can be explained by the adsorption of the amines which leads to a decrease of $Cu^{2+}$ ions concentration at the electrode interface. An important feature is the peak potential shift toward more positive values, in the presence of amines in the electrolyte solution, determined by the change of the diffusion layer thickness. According to literature data [22, 23] for reversible or quasi-reversible systems, such as $Cu^{2+}/Cu^{+}/Cu^{0}$, a quantitative interpretation is possible according to Randles-Sevcik equation:

$$I = (2.687 \times 10^5) \cdot n^{\frac{3}{2}} \cdot v^{\frac{1}{2}} \cdot D^{\frac{1}{2}} \cdot A \cdot C \qquad (1)$$

where: $I$ is the cathodic peak current for $Cu^{2+}$ ions reduction; $n$ is the number of electrons involved in the redox reaction (in this case n = 1); $v$ is the scan rate, V s⁻¹; $D_{Cu^{2+}}$ is the diffusion coefficient, cm² s⁻¹; $A$ is the electrode surface area, cm²; and $C$ is the active species concentration in the electrolyte solution, mol cm⁻³.
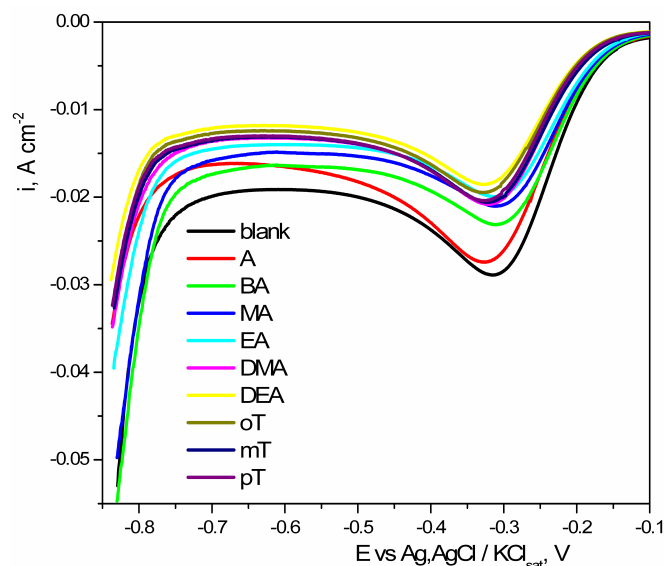


Figure 1. Influence of organic amines on the cathodic peak current for $Cu^{2+}$ ions reduction from acid electrolyte solution (20 g L⁻¹ $Cu^{2+}$, 1.86 mol L⁻¹ H₂SO₄, 50 ppm Cl⁻), at 10 mV s⁻¹ scan rate.

In Fig. 2 the influence of the scan rate on the cathodic peak current is presented. The main effect of the scan rate is the shift of the cathodic peak potential to more negative values and the increase of the cathodic peak current. According to equation (1) the peak current is proportional to the bulk ion concentration and to the square root of the scan rate, indicating that the electrode reaction is controlled by mass transport.

The mass transport of $Cu^{2+}$ ions from the bulk of the solution to the electrode surface is assured by a convective diffusion mechanism. Diffusion appears because of the concentration gradient between bulk and interface concentration, while convection appears because of the density gradient between bulk and interface electrolyte solution density [19]. As shown in literature [24-26] the presence of organic compounds in the electrolyte solution doesn't change the electrodeposition mechanism. However, interfacial viscosity is changed, and accordingly the diffusion of the active species ($Cu^{2+}$ ions) decreases.

The dependence of the peak current ($I$) versus the square root of the scan rate ($v^{1/2}$) shown in Fig. 3 is a straight line, indicating that the process is exclusively controlled by diffusion. From this representation the diffusion coefficient $D_{Cu^{2+}}$ of the oxidizing species can be determined with high precision.
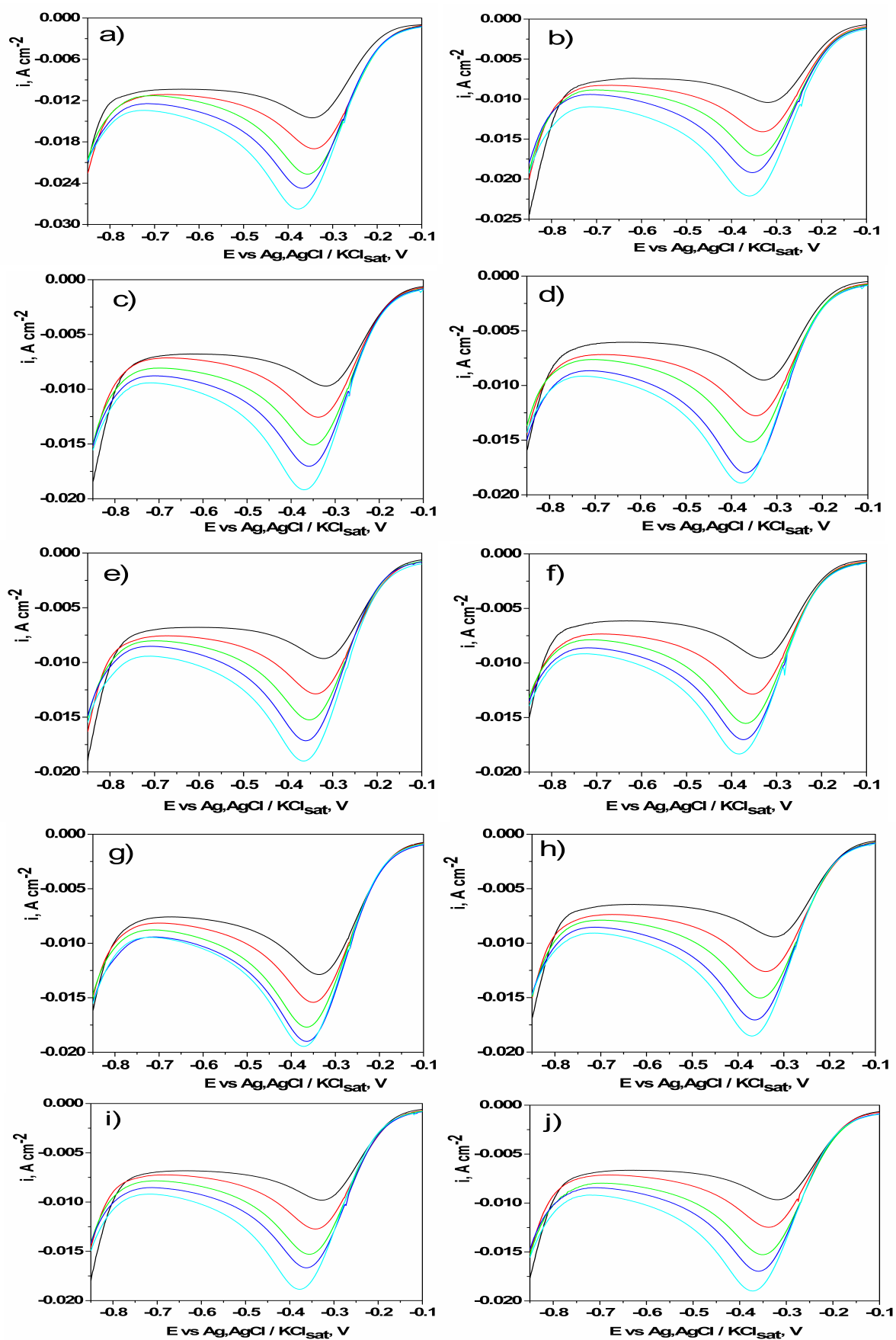
Figure 2. Scan rate influence on the cathodic peak current ($-$ v = 10 mV s$^{-1}$, $-$ v = 20 mV s$^{-1}$, $-$ v = 30 mV s$^{-1}$, $-$ v = 40 mV s$^{-1}$, $-$ v = 50 mV s$^{-1}$), for Cu$^{2+}$ ions reduction from unstirred blank solution (a) and from solutions containing 1 ml L$^{-1}$ of A (b); BA (c); MA (d); EA (e); DMA (f); DEA (g); *o*T (h); *m*T (i) and *p*T (j).
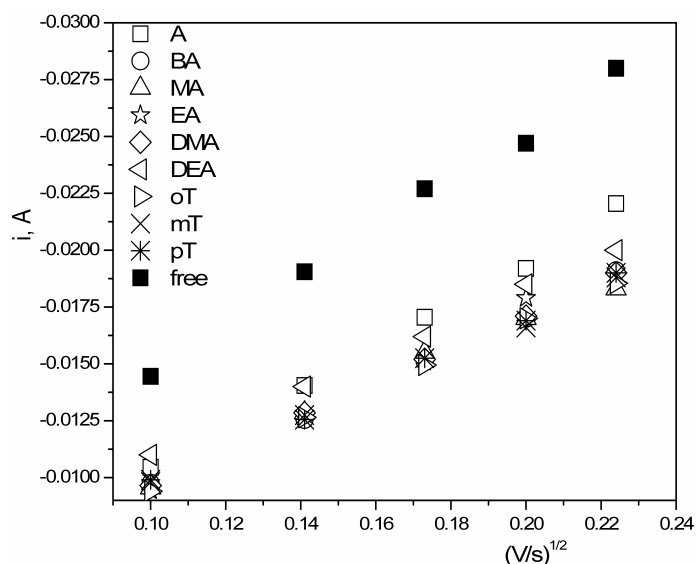
Figure 3. Dependence of the peak current on the square root of the scan rate for $Cu^{2+}$ ions reduction from acid solution (20 g L$^{-1}$ Cu$^{2+}$, 1.86 mol L$^{-1}$ H$_2$SO$_4$, 50 ppm Cl$^-$) in the presence of organic amines.

*TABLE 1. Fitting results of current peak versus $v^{1/2}$ dependence and calculated diffusion coefficients*

| Amine | slope | intercept | $R^2$ | $D_{Cu^{2+}} \cdot 10^6$ [cm$^2$ s$^{-1}$] |
|-------|-------|-----------|-------|--------|
| blank | 105.43 | $-4.27 \times 10^{-3}$ | 0.998 | 6.21 |
| A | 92.02 | $-1.14 \times 10^{-3}$ | 0.998 | 4.73 |
| BA | 75.14 | $-2.11 \times 10^{-3}$ | 0.999 | 3.15 |
| MA | 81.75 | $-5.41 \times 10^{-3}$ | 0.997 | 3.73 |
| EA | 78.45 | $-1.68 \times 10^{-3}$ | 0.999 | 3.44 |
| DMA | 74.82 | $-2.22 \times 10^{-3}$ | 0.999 | 3.13 |
| DEA | 73.28 | $-7.30 \times 10^{-3}$ | 0.999 | 2.98 |
| $o$T | 73.01 | $-2.11 \times 10^{-3}$ | 0.999 | 3.06 |
| $m$T | 71.18 | $-2.71 \times 10^{-3}$ | 0.998 | 2.83 |
| $p$T | 73.23 | $-2.45 \times 10^{-3}$ | 0.999 | 2.99 |

The result shown in Table 1, obtained by linear regression, indicate that the addition of amines to the electrolyte solution leads to a decrease of the slope compared to the blank solution, due to their adsorption on the electrode surface. The adsorption of the amines shields the electrode surface and blocks the $Cu^{2+}$ ions diffusion towards the interface.

Since the experimental measurements are carried out at high $Cu^{2+}$ concentration in unstirred electrolyte solutions, it can be assumed that the $Cu^{2+}$ ions transport from bulk to the electrode surface takes place only by diffusion. Diffusion is determined by a concentration gradient between bulk ($C^*_{Cu^{2+}}$) and interface concentration ($C_{Cu^{2+}}$). The idea that, the electrolyte solution is strongly acidified (1.86 mol L$^{-1}$ H$_2$SO$_4 \approx$ pH = 0), as is shown in the literature [27], it can be assumed that the only metallic ions which can reach to the electrode surface are $Cu^{2+}$ ions ($C^*_{Cu^+} \approx 0$).

Fig. 4 shows the chronoamperometric curves obtained in the blank solution and in the presence of aromatic amines. The current density versus time dependencies were recorded after holding the electrode for 10 seconds at a potential where no electrochemical processes take places (E = 0.0 V) followed by stepping the potential to E = -0.25 V for 100 seconds. The shape of the applied potential step is given as inset in Fig. 4. The potential step causes a sudden increase of the current density due to $Cu^{2+}$ ions diffusion from bulk to the electrode interface [28]. The immediate decrease of current density corresponds to $Cu^{2+} \rightarrow Cu^+$ reduction and to $Cu^+$ ions accumulation in the electrochemical double layer.

The maximum amount of $Cu^+$ ions formed in the electrochemical double layer corresponds to the constant current density reached at the end of the potential step. Since the reduction of $Cu^+$ to metallic copper ($Cu^+ \rightarrow Cu^0$) is considered to be the fast step [29-31], it can be assumed that the time needed to form a metallic copper layer is proportional to the diffusion time of $Cu^{2+}$ toward the electrode interface [10]. Even if there is a concentration gradient, the presence of Cl$^-$ ions prevents the $Cu^+$ ions diffusion into the bulk by forming CuCl$_{(s)}$, and the current remains constant in time (Fig. 4). The amount of formed $Cu^+$ would be the same as the amount of $Cu^+$ reduced to metallic copper.
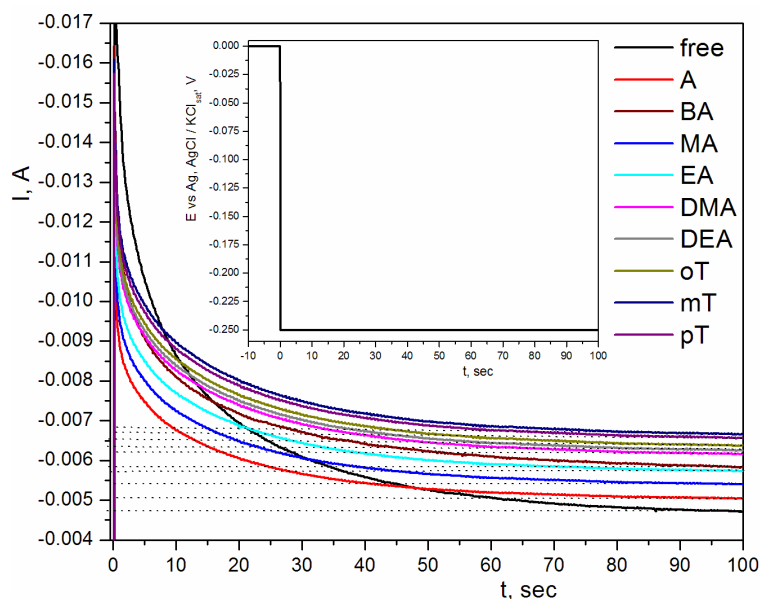
Figure 4. Current - time dependencies for $Cu^{2+}$ ions reduction, in the absence and presence of 1 mL L$^{-1}$ added amine, for a potential step at E = - 0.25 V.

The presence of amines in the electrolyte solution leads to a decrease of the cathodic current recorded at $\tau = 0$ s when the step potential is applied. This can be explained as a result of the diminished $Cu^{2+}$ ions concentration at the interface, due to the adsorption of protonated amines molecules, as it has been confirmed for thiourea [32] and 3-mercapto-1-propansulfonate sodium salt [33]. At the end of the potential step, the cathodic current in the presence of amines is higher than in the blank solution and this corresponds to a decrease of the real electrode surface due to its covering by adsorbed molecules [6]. The influence of chloride ions can not be excluded, since they accelerate the $Cu^{2+}$ reduction process even in the presence of amines.

As discussed above, reaching the constant current value corresponds to a maximum loading with $Cu^+$ ions. The moment $\tau$ when this maximum loading is reached corresponds to the moment when the copper metal layer formation begins. As it can be seen, this moment decreases from around 90 seconds in the absence of additives in the electrolyte solution, to around 10 seconds in the presence of toluidines.

This can be related to the degree of electrode surface coverage, which on turn depends on the coverage volume of the amines molecules. A smaller molecule corresponds to a smaller coverage degree and hence to a lesser reducing time (the effective time reported to the covered electrode surface). Larger coverage degrees correspond to a smaller difference time ($\Delta\tau$) for $Cu^{2+}$ reducing process.

From relation (2) [23], taking into account that, at $\tau$ time the $C^*_{Cu^+} \approx 0$ (all these ions are rapidly reduced to metallic copper), the diffusion layer thickness $\delta$ at the moment $\tau$ can be estimated, using the diffusion coefficient values calculated $D_{Cu^{2+}}$ above.

$$i(\tau) = -\frac{n \cdot F \cdot D_{Cu^{2+}} \cdot C^*_{Cu^{2+}}}{\delta(\tau)} \quad (2)$$

where: $n$ is the number of electrons involved in the redox reaction (in this case n = 1); $F$ is the Faraday constant, 96 486 C mol$^{-1}$; $D_{Cu^{2+}}$ is the diffusion coefficient, cm$^2$ s$^{-1}$ and $\delta$ is the diffusion layer thickness, μm;

TABLE 2. *Diffusion layer thickness values for copper electrodeposition from acidic electrolyte solution in the presence of various added amines (1 mL L$^{-1}$)*

| Amines | $\Delta\tau$ [s] | $-i(\tau)$ [mA] | $\delta$ [μm] |
|---|---|---|---|
| blank | - | 4.71 | 40 |
| A | 47 | 5.05 | 28 |
| BA | 18 | 5.92 | 16 |
| MA | 32 | 5.39 | 21 |
| EA | 22 | 5.74 | 18 |
| DMA | 14 | 6.17 | 15 |
| DEA | 13 | 6.32 | 14 |
| $o$T | 12 | 6.42 | 14 |
| $m$T | 8 | 6.57 | 13 |
| $p$T | 10 | 6.70 | 14 |

The data presented in table 2 shows that the addition of organic compounds to the electrolyte solution leads to a decrease of the diffusion coefficient and of the diffusion layer thickness, due to the higher $i(\tau)$ values determined by higher degrees of surface coverage. It can observed that, the presence of $m$T in the electrolyte solution determines an almost three times decrease of the diffusion coefficient and of the diffusion layer thickness. Similar effects have been also obtained for BA, probably because of the methyl group attached to the amino group and not directly to the benzene as in case of all other amines used in this study.

# 4. Conclusions

The diffusion coefficient of $Cu^{2+}$ ions and the diffusion layer thickness have been determined for copper electrodeposition from acidic electrolyte solution in the presence of aromatic amines, by linear sweep voltammetry and chronoamperometry.

The results showed that, if 1 mL $L^{-1}$ aromatic amine is added into the electrolyte solution, the effect is to decrease the diffusion coefficient and the diffusion layer thickness. The most obvious changes have been obtained for $m$T: the diffusion layer thickness decreased from 40 µm in the absence of $m$T to 13 µm in the presence of $m$T. It can be concluded that the modification of the diffusion layer thickness depends on the nature of the organic additives, particularly on their electronic properties [11,14] and also molecular volume.

Decreasing of both diffusion coefficient of $Cu^{2+}$ ions and diffusion layer growth represents a semi-quantitative measure for the inhibitory effect of added amines.

## ACKNOWLEDGEMENTS

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