

# Magnetic Effect during Copper Electrodeposition: Diffusion Process Considerations

P. Fricoteaux,\* B. Jonvel, and J.-P. Chopart

DTI, CNRS-UMR 6107, Université de Reims, B.P. 1039, 51687 Reims Cedex 2, France

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The copper electrodeposition from a sulfuric acid solution under magnetic field influence has been investigated. Results show that the apparent modifications of current–overpotential curves in the kinetic domain deal with modifications of a real electrode surface. An original cell able to jam the magnetoconvection was used to demonstrate that only a convective effect appears during copper plating under a magnetic field. A new relationship of the limiting current that takes into account the involved electron number to the power 4/3 and the kinematic viscosity to the power  $-2/3$  can be established.

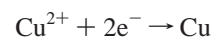
## Introduction

Magnetoelectrochemistry (MEC), i.e., electrochemistry with a magnetic field superimposed on the electrochemical apparatus, gives opportunities for obtaining either new materials or deeper information on electrodeposition mechanisms. Over thirty years, numerous papers have shown the assets of this method. The best known effect is an increase of diffusion currents due to a magneto-induced convection<sup>1–4</sup> when the magnetic field lines are parallel to a plane working electrode. This magnetically induced convective effect is now well-known and relevant to magnetohydrodynamic (MHD) science. In electrochemical reactions, although MHD effects are less effective than those obtained with classical mechanical systems (e.g., rotating electrode), stationary currents can be obtained with good accuracy; therefore the knowledge of electrochemical mechanisms can be improved. Modulation of the superimposed magnetic field causes modulation of the electrochemical current, and a new transfer function can be obtained by the ratio of these two modulations.<sup>5</sup> Electrocrystallization of zinc in a basic media has been studied by these techniques, allowing for the first time the retrodiffusion of the hydroxide ions from the cathode<sup>6</sup> to be highlighted.

The magnetic convection can create modification of texture or also generate structural effects such as an improved smoothness of electrodeposited metals. This last effect has led many experiments to be undertaken, aiming at obtaining smooth materials from an inhibitor-free electrolyte.<sup>7,8</sup>

Due to its industrial interest, copper electrodeposition is one of the most studied systems in MEC. Another interesting point is the fact that Cu electrocrystallization can be controlled: co-deposition of hydrogen can be avoided, and dendritic growth is not too drastic if experiments are conducted cautiously. Papers on this topic have aimed at analyzing the magnetically induced modifications on the deposit texture,<sup>9</sup> but also on electrochemical kinetics.<sup>10–12</sup> Moreover, many experiments carried out with copper without magnetic field comparisons are easier. The major results reported on copper electrodeposition or electrodisolution revealed a two-step transfer mechanism.<sup>12–15</sup> For very low overpotentials the two steps are charge-transfer controlled, but mass transport exerts quite rapidly an effect on the current when cathodic overpotential increases.

One last point must be emphasized: for the  $\text{Cu}^{2+}/\text{Cu}$  system in sulfuric solution and high cathodic overpotential, during the transfer reaction



no adsorption process occurs and therefore the limiting current is under diffusion control only. For some metallic electrodepositions this last condition is not fulfilled and these cases have to be disregarded to investigate transport phenomenon. For example, during silver electrodeposition some adsorption steps can occur and, therefore, the current is not merely diffusive.<sup>16</sup> This adsorption effect can be responsible for mistakes in determining the silver ion diffusion coefficient.<sup>17</sup>

Prior to 1983, the first works devoted to the copper system under magnetic control showed the mass-transport effects to increase the limiting currents and induce modifications of the deposit structure. Some of these works led to the first theoretical approaches in magnetohydrodynamics (MHD).<sup>18–20</sup>

Additional investigations concerning electrodes parallel to the magnetic induction lines<sup>10,21</sup> have shown that the classic MHD relationships<sup>22</sup> could well be used to account for the increase of limiting currents. Determination of the preferred orientations of Cu deposits under magnetic conditions<sup>9</sup> highlighted mass-transport control as found in the usual hydrodynamic conditions, e.g., a rotating disk.

A magnetic field can induce modifications on nonsteady behavior as current vs time curves.<sup>23–25</sup> Magnetic effects on kinetic parameters of either electrochemical or chemical steps have been evoked, though no conclusive evidence has never been given.

An analysis of the current–overpotential curves for the electrodeposition of copper from sulfuric acid solution has led to the conclusion that magnetic fields up to 0.9 T do not alter the cathodic charge-transfer coefficient.<sup>10</sup> The authors concluded on the modifications of the exchange current density by alteration of the true geometric surface of the working electrode. As further evidence, Fricoteaux et al., using a radiotracer, have shown that no detectable change of the exchange current density was induced by a 0.4 T magnetic field.<sup>26</sup> On the contrary, very high magnetic fields could allow detection of effects not appearing in weak magnetic induction. This could explain the important decrease of the exchange current reported by Yamanaka et al.<sup>27</sup> when a magnetic field of 13 T was used. In

\* Corresponding author. E-mail: patrick.fricoteaux@univ-reims.fr.

that case, the remaining question is to know whether there is a threshold value for the magnetic amplitude, to determine it, and to explain the reason for its existence. Despite the papers quoted above, Noninski<sup>11</sup> later argued a 1.2 T magnetic field was responsible for alteration of the copper deposition rate in a region he assumed to be transfer controlled. In such a case, the magnetic field induces modifications of the exchange current or charge-transfer coefficient in at least one of the two steps of the mechanism involved.

Actually, the bibliography on electrochemistry under a magnetic field shows that many questions have to be resolved, one of them being the relationship of the limiting current versus the superimposed magnetic field. Recently, Leventis et al.<sup>4</sup> have found an experimental relationship and Olivier et al.<sup>28</sup> have suggested a theoretical one for the MHD limiting current. In ref 4, only soluble species were used; therefore the problem now has to be solved in the case of copper deposit. Previous results<sup>10,12</sup> highlighted the empirical MHD relationship between the limiting current and  $B^{1/3}C^{*4/3}$ , in which  $B$  is the magnetic field amplitude and  $C^*$  is the bulk concentration of copper(II) species,<sup>19,22</sup> but the effects of viscosity and some other parameters have not been quantified yet. A good understanding of limiting current rules for copper deposition is important to understand phenomena of electrodeposition and to produce some composite structures such as multilayers. For example, with Cu/Ni multilayers<sup>29</sup> or Cu/Co multilayers,<sup>30</sup> the reduction of copper was realized by potentiostatic techniques under mass-transport control. As those multilayers are produced for their expected magnetic properties (Giant Magnetoresistance), some preparations may have to be realized under magnetic induction.

This paper deals with copper electrodeposition kinetics and the experimental relationship of the limiting current under a moderate (0–1 T) magnetic field. The convective effects studied in this paper have already been verified, but experimental works have also been undertaken on this topic to account for magnetic effects on charge-transfer steps.

## Experimental Details

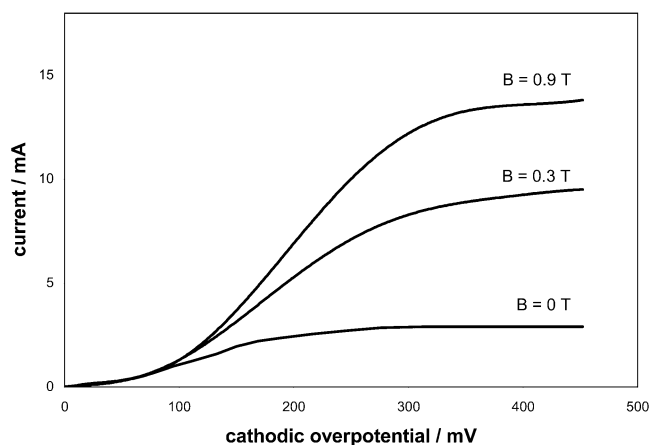
All chemical products used were p.a. grade reagents (Merck or Prolabo). The solutions were prepared with twice distilled water and were made of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with  $\text{H}_2\text{SO}_4$ , or glycerol. Concentrations were ranged from  $10^{-2}$  to  $0.75 \text{ mol L}^{-1}$  for  $\text{Cu}^{2+}$ , 0.9 to  $4.0 \text{ mol L}^{-1}$  for  $\text{H}_2\text{SO}_4$ , and 1.1 to  $5.3 \text{ mol L}^{-1}$  for glycerol. Before electrodeposition, nitrogen bubbling deoxygenated the solution. During electrodeposition, the cell was maintained at a constant temperature by circulation of thermostated water through a double wall.

A conventional three-electrode cell has been used. The working electrode was a vitreous carbon disk (o.d. = 3 mm). The reference electrode was  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4(\text{sat.})$ . The counter electrode was a large area copper plate ( $4 \text{ cm}^2$ ).

For MEC experiments the whole cell was immersed in the gap of an electromagnet (DRUSCH EAM 20G). The 20-cm diameter cylindrical pole pieces of this magnet can generate a controlled and regulated magnetic field on the whole gap by a Hall effect probe control that was introduced in the gap. No variation more than 1 mT amplitude can be obtained for a 5-cm displacement from the center of the pole pieces.

The electrolytic resistance was determined by means of an impedance measurement technique, and overpotentials were corrected for the ohmic drop before current–overpotential curves were plotted.

Before the current–overpotential curve was plotted, a copper predeposit was prepared with constant cathodic overpotential



**Figure 1.** Current vs cathodic overvoltage for copper electrodeposition. Conditions: Cu electrode, diameter = 3 mm;  $[\text{CuSO}_4] = 0.5 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 1.8 \text{ mol L}^{-1}$ ;  $T = 298 \text{ K}$ .

value (typically  $-130 \text{ mV}$ ), over about 10 min and outside the electromagnet gap. The predeposit was achieved when the current was stationary and had a constant value for each predeposit. With such a technique, we were sure that we would carry out experiments with an unchanged electrode area, because it has been highlighted<sup>13</sup> that the preparation of the working electrode surface exerts a dramatic influence upon experimental values such as exchange current densities and double layer capacities. The electrodeposition was achieved using a Solartron 1286 potentiostat. To carry out potential sweeps, the potential sweep rate was chosen so that the measured current values could be seen as stationary ones, and the electrode surface increase could be avoided. Typically the sweep rate was  $1 \text{ mV/s}$ . When a set of experiments was achieved, a new measurement of the steady current was made with the same experimental conditions that were used for the predeposit. If this new value was not equal to the first one, the involved experiments were disregarded and a new set was realized.

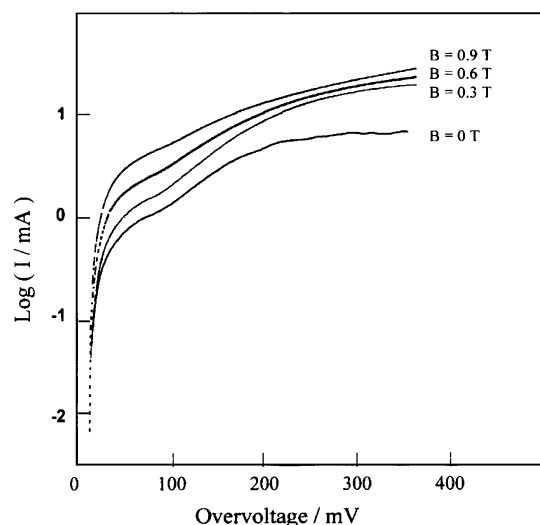
## Results and Discussion

**Discrimination between Surface, Kinetics and Convective Effects.** Figure 1 shows an example from our results with copper deposition. The magnetically induced enhancement of current density is obvious as soon as the cathodic overpotential is higher than  $80 \text{ mV}$ . According to the experimental conditions viz. electroactive species concentration, a limiting current diffusion can be obtained (Figure 1), but with the same experimental conditions as in ref 11 (i.e.,  $\text{CuSO}_4$   $0.75 \text{ M}$  and  $\text{H}_2\text{SO}_4$   $2 \text{ M}$ ) it is not yet possible (Figure 2). In this last case, the superimposition of a magnetic induction alters the current over the whole cathodic overpotential domain. The limiting current  $I_{\text{lim}}$  increases, but for magnetic fields higher than  $0.3 \text{ T}$  no limiting current can be reached owing to the rate surface evolution, and therefore, the logarithmic relationship between the current and the overpotential  $\eta$  is modified when  $\eta$  ranges between  $-100$  and  $-150 \text{ mV}$ .

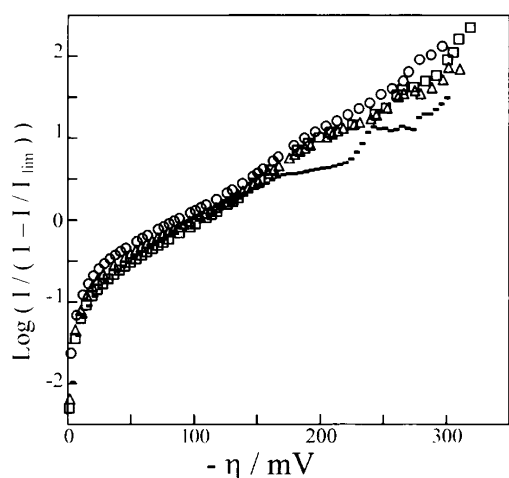
$$\eta = E_{\text{applied}} - E_{\text{eq}}$$

where  $E_{\text{eq}}$  is the experimental equilibrium Nernst potential.

Here we find the same results as reported in ref 11. However, major comments on these plots have to be stressed. First, the domain up to  $100 \text{ mV}$  cathodic overpotential cannot be considered as a Tafel region because such an assertion would mean that the limiting current has to be more than 10 times higher than the highest current in the assumed Tafel region.



**Figure 2.** Current vs cathodic overvoltage for copper electrodeposition. Conditions: Cu electrode, diameter = 3 mm;  $[\text{CuSO}_4] = 0.75 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 2 \text{ mol L}^{-1}$ ;  $T = 303 \text{ K}$ .



**Figure 3.** Logarithmic representation of current (mA) vs cathodic overvoltage ( $-\eta$ ) for copper electrodeposition with mass-transport correction.  $I_{\text{lim}}$  is the diffusion limiting current. Conditions: Cu electrode, diameter = 3 mm;  $[\text{CuSO}_4] = 0.1 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol L}^{-1}$ ;  $T = 303 \text{ K}$ . Key: (—)  $B = 0 \text{ T}$ ; ( $\square$ )  $B = 0.3 \text{ T}$ ; ( $\Delta$ )  $B = 0.6 \text{ T}$ ; ( $\circ$ )  $B = 0.9 \text{ T}$ .

Actually, the limiting current without magnetic field is very rapidly reached and a logarithmic relationship between overpotential and current does not evidence a kinetic transfer control. As a matter of fact, it is necessary to take into account the mass-transport phenomenon, which was not done in ref 11 where the limiting currents  $I_{\text{lim}}$  were not reported. To get an accurate analysis of the effects of a magnetic field higher than 0.3 T onto copper electrodeposition, a  $\text{CuSO}_4$  concentration lower than 0.75 M has to be used to avoid excessive current densities, which would make it impossible to reach limiting currents by modification of the true geometric area as mentioned above.

When taking into account mass-transport phenomenon, no modification of kinetic parameters can be deduced for magnetic fields up to 0.9 T (Figure 3). With such experimental cares, kinetic parameters can be calculated for many Cu(II) concentrations and magnetic fields.

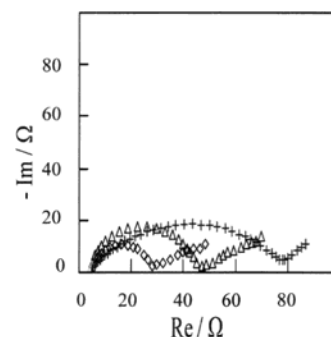
When mass transport is not taken into account, the current density is expressed as

$$\log j = \log j_0 - b\eta \quad (1)$$

**TABLE 1: Exchange Current Densities and Tafel's Coefficients for the System  $\text{Cu}^{2+}/\text{Cu}$ <sup>a</sup>**

	determination with eq 1			determination with eq 2		
	0.1 mol L <sup>-1</sup>	0.15 mol L <sup>-1</sup>	0.2 mol L <sup>-1</sup>	0.1 mol L <sup>-1</sup>	0.15 mol L <sup>-1</sup>	0.2 mol L <sup>-1</sup>
Exchange Current Density/ $\text{mA cm}^{-2}$						
$B = 0 \text{ T}$	5.8	6.2	6.4	5.9	4.8	5.2
$B = 0.3 \text{ T}$	6.1	5.5	7.8	5.0	4.4	5.8
$B = 0.6 \text{ T}$	6.8	5.8	7.9	5.8	4.7	6.2
$B = 0.9 \text{ T}$	7.6	6.2	9.9	6.2	5.0	8.6
Tafel's Coefficient/ $\text{V}^{-1}$						
$B = 0 \text{ T}$	5.5	5.3	6.2	8.7	11.0	11.6
$B = 0.3 \text{ T}$	6.0	7.0	6.7	10.3	11.1	10
$B = 0.6 \text{ T}$	5.6	7.1	6.2	9.3	11.4	9.8
$B = 0.9 \text{ T}$	5.3	6.7	5.3	9.6	10.3	9.2

<sup>a</sup> Values have been calculated from experimental current vs overpotential curves by taking into account the mass-transport process (eq 2) or not (eq 1).



**Figure 4.** Impedance diagrams in Nyquist plot for the Cu(II)/Cu system during electrodeposition. Conditions:  $[\text{CuSO}_4] = 0.75 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 2 \text{ mol L}^{-1}$ ;  $B = 0.6 \text{ T}$ ;  $T = 303 \text{ K}$ . Overvoltage: (+)  $-35 \text{ mV}$ ; ( $\Delta$ )  $-135 \text{ mV}$ ; ( $\diamond$ )  $-235 \text{ mV}$ .

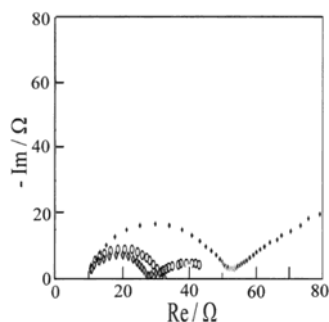
where if the mass-transport phenomenon is taken in account and limited diffusion current is available, one obtains

$$\log[j/(1 - j/j_{\text{lim}})] = \log j_0 - b\eta \quad (2)$$

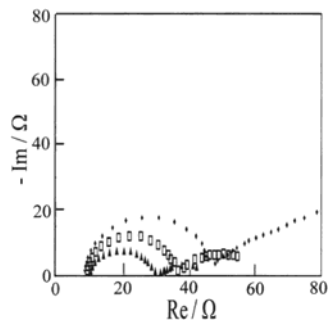
Table 1 summarizes the Tafel coefficient  $b$  and the exchange current density  $j_0$  values for various copper(II) concentrations and magnetic field amplitudes (even though these parameters are not totally meaningful because the electrodeposition mechanism was proved not to be a mere one-step electronic transfer,<sup>14,15</sup> they can be used to evaluate the kinetic process).

Without a magnetic field, the Tafel slopes and apparent exchange current density values are in agreement with those of refs 28 and 30; the values obtained with a superimposed magnetic field and low copper(II) concentrations allow us to conclude there is no magnetically induced effect on copper transfer parameters. Tafel slopes and apparent exchange current densities have to be regarded as constant with magnetic field up to 1 T. Surface effects have to be considered to explain tenuous differences for concentration higher than  $0.15 \text{ mol L}^{-1}$ .

In Figure 4, electrochemical impedance spectra of the copper electrode are reported in the Nyquist plane for the electrolytic conditions of ref 11, with various overpotentials and a 0.6 T magnetic field. For a low overpotential ( $-35 \text{ mV}$ ), a flattened loop is obtained in the high-frequency domain. That is the typical response of the two-step mechanism with soluble intermediate species.<sup>14,15,31</sup> For low frequencies, a straight line whose slope is very close to  $45^\circ$  evidences a diffusion process previously highlighted by Krzewska<sup>15</sup> for cathodic overpotentials lower than 100 mV. For more negative overpotentials, the Warburg line



**Figure 5.** Impedance diagrams in Nyquist plot for the Cu(II)/Cu system during electrodeposition. Conditions:  $[\text{CuSO}_4] = 0.2 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol L}^{-1}$ ; overvoltage  $\eta = -150 \text{ mV}$ ;  $T = 303 \text{ K}$ . Key: (♦)  $B = 0$ ; (○)  $B = 0.3 \text{ T}$ ; (◇)  $B = 0.9 \text{ T}$ .



**Figure 6.** Impedance diagrams in Nyquist plot for the Cu(II)/Cu system during electrodeposition. Conditions:  $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol/L}$ ; overvoltage  $\eta = -150 \text{ mV}$ ;  $T = 303 \text{ K}$ ;  $B = 0.3 \text{ T}$ .  $[\text{CuSO}_4]$ : (♦)  $0.1 \text{ mol L}^{-1}$ ; (□)  $0.15 \text{ mol L}^{-1}$ ; (▲)  $0.2 \text{ mol L}^{-1}$ .

still exists and the high-frequency loop becomes a semicircle that indicates the kinetic predominance of one step of the charge transfer.

Once more, convective effects of magnetic induction can be deduced for smaller concentrations of electroactive species Cu(II). For a constant overpotential ( $-150 \text{ mV}$ ), current increases with  $B$  whereas the low-frequency loop amplitude decreases as the magnetic field increases (Figure 5), implying that the diffusion layer thickness decreases. At the same time, the high-frequency loop amplitude decrease with  $B$ . This fact is in accordance (when the anodic component of the current can be neglected<sup>14</sup>), with the  $R_{ct}I$  product that is expressed as

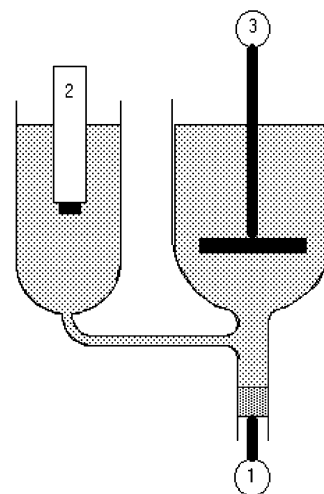
$$R_{ct}I = 2RT/F(b_1 + b_2)$$

The electroactive concentration species effect is expressed by Figure 6, where impedance diagrams are reported for constant magnetic field and overpotential and various concentrations of Cu(II) species. The decrease of the low-frequency loop amplitude indicates, as above, the decrease of the diffusion layer thickness. Such a fact agrees with results<sup>3,4,10,22,32</sup> that have established that the magnetic convective effect is all the more effective as the product  $BC^*$  is greater ( $C^*$  is the bulk concentration of the electroactive species, i.e., Cu(II)).

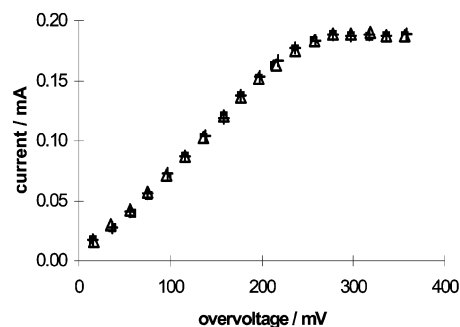
Considering the results of these preliminary experiments, there is no obvious evidence of the reported magnetically induced kinetics effects.<sup>11</sup>

Furthermore, to study only the mass-transport effect, we have to ensure that the whole current–potential curve is not altered by magnetic field when no convection occurs.

As the current increase comes from convective force, it is obvious that movements of solution exist during magnetoelectrolysis. So, if we jam any movement parallel to the surface, we can suppose that enhancement of limiting current vanishes.



**Figure 7.** Electrochemical cell with the working electrode embedded in a glass pipe: (1) working electrode; (2) reference electrode; (3) counter electrode.



**Figure 8.** Current vs cathodic overvoltage for copper electrodeposition. Conditions: Cu electrode, diameter = 3 mm;  $[\text{CuSO}_4] = 0.05 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 1.8 \text{ mol L}^{-1}$ ;  $T = 298 \text{ K}$ . Key: (+)  $B = 0 \text{ T}$ ; (Δ)  $B = 0.9 \text{ T}$ .

To prove that, we have used an original cell, in which the working surface was embedded in a glass pipe (Figure 7). Results of current versus overpotential curves are plotted in Figure 8. Because no modification of current–potential curves has been detected, we could conclude that the use of a magnetic field did not modify kinetics parameters and that the  $\text{Cu}^{2+}/\text{Cu}$  system was relevant to study the magnetic field effect on mass transport.

**Magnetoconvection Analysis.** As quoted above, the most obvious effect of the superimposition of a constant magnetic field parallel to a plane-working electrode is a convective current density increase. This effect is generally assumed to be the consequence of the Lorentz force that acts on the current density. Fahidy<sup>20</sup> has presented a first theoretical approach. The force creates convection near the working electrode and leads to a modification of the diffusion layer, as shown experimentally by O'Brien et al. with a laser interferometer technique.<sup>33</sup> Later, additional investigations by Aaboubi et al.<sup>22</sup> concerning horizontal electrodes, parallel to the magnetic induction lines, have shown that classic MHD relationships could well be used to account for the increase of limiting currents. From theoretical considerations based on Mollet et al.,<sup>34</sup> they have found a relationship between limiting diffusion current on a disk electrode and superimposed magnetic field amplitude, which is expressed by

$$I_{\text{lim}} = 0.678nFD^{2/3}d^{5/3}C^*\alpha^{1/3} \quad (3)$$

in which  $F$  is the Faraday constant,  $d$  is the diameter of the



**TABLE 2: Comparison of Limiting Diffusion Currents Calculated with Various MHD Relationships for the Same Experimental Conditions as Figure 1**

<i>B</i> /T	<i>I</i> <sub>lim</sub> /mA			
	expt	from eq 5	from eq 6	from eq 12
0.3	9.5	3.8	6.7	9.2
0.9	13.8	5.4	9.6	13.2

electrode,  $C^*$  is the bulk concentration,  $D$  is the diffusion coefficient of the electroactive species,  $n$  is the number of electrons involved in the electrochemical reaction, and  $\alpha$  is the tangential velocity gradient  $\alpha = \partial v_y / \partial x$  in which  $y$  and  $x$  are respectively the tangential and normal to the electrode surface coordinates. It must be noticed that in ref 22 the only electrochemical system used involved an  $n$  value equal to 1.

They have experimentally shown that

$$\alpha = kBC^* \quad (4)$$

with  $k$  an empirical constant, which was found to be equal to  $0.16 \text{ m}^3 \text{ T}^{-1} \text{ s}^{-1} \text{ mol}^{-1}$  with a ferro–ferricyanide electrochemical system.

Therefore, in this case, the eq 3 can be rewritten as

$$I_{\text{lim}} = 0.45nFD^{2/3}A^{5/6}C^{*4/3}B^{1/3} \quad (5)$$

in which  $A$  is the surface of the electrode.

More recently, Leventis et al. have presented a new relationship to account for the limiting current increase.<sup>4,35</sup> With other electrochemical systems, they have determined the different exponents in comparison with the equation of ref 22 and they have introduced other parameters such as kinematic viscosity. They obtained the empirical relationship (6).

$$I_{\text{lim}} = 431n^{3/2}FB^{1/3}A^{3/4}DC^{*4/3}\nu^{-1/4} \quad (6)$$

The exponents of term  $B$  and  $C^*$  experimentally determined are the same in refs 4 and 5, and the  $A$  exponent in eq 6 is not very different from the one in eq 5; the gap between the two values is only 1/12. It has to be noticed that the theoretical 5/6 value (eq 5) was verified by Aaboubi<sup>36</sup> for a diameter greater than 1 mm, and less than 10 mm. The 3/4 exponent of eq 6 has been experimentally determined by a log–log regression for only 3 diameters (1.6, 4.5 and 5 mm). In ref 5 the viscosity was not considered and the theoretical  $D$ -exponent was not experimentally determined.

Here, our main purpose is to test the validity of eq 5 for copper electrodeposition with the same hypotheses as in ref 22 but considering the kinematic viscosity and the number of involved electrons as it has been done in ref 4.

Like Aaboubi et al.<sup>22</sup> and Leventis et al.<sup>4</sup> our results with copper plating correspond to the rule as  $B^{1/3}C^{*4/3}$ , and an example of limiting current increasing with magnetic induction was already produced in Figure 1. However, current values obtained by extrapolation of Aaboubi et al.'s equation (5) and those obtained by Leventis et al.'s equation (6) diverge and do not coincide with our present experimental results. Calculations corresponding to the limiting currents from Figure 1 were presented in Table 2. Parameters were  $A = 7.1 \times 10^{-6} \text{ m}^2$ ,  $\nu = 1.26 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ,  $D = 5.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  extracted from ref 37, and  $C^* = 500 \text{ mol m}^{-3}$ .

Regarding eq 6, values diverge from experimental results by a factor of 2 and for eq 5, by a factor of 3. However, kinematic viscosity was not included in the last relationship and no effect of the  $n$  value could be taken into account because of its sole

**TABLE 3: Kinematic Viscosity of Electrolytes, Diffusion Coefficients of Copper(II) Ion and  $k''$  Obtained by  $k'' = I_{\text{lim}}/n^{4/3}FD^{2/3}A^{5/6}C^{*4/3}B^{1/3}$** 

	$\text{H}_2\text{SO}_4$				glycerol			
$10^6\nu/\text{m}^2 \text{ s}^{-1}$	1.130	1.261	1.457	1.718	1.263	1.882	2.839	4.005
$10^{10}D/\text{m}^2 \text{ s}^{-1}$	6.16	5.59	4.64	4.03	5.92	4.02	2.95	2.08
$10^2k''/\text{MKSA}$ unity	45.4	43.0	39.6	34.6	42.9	33.1		

value equal to 1. So we have worked from their hypotheses but introduced the two supplementary parameters.

Relationship (3) from Aaboubi et al.<sup>22</sup> derives from the one of Mollet et al.<sup>34</sup> It was argued in ref 22 that the velocity gradient at the electrode was directly proportional to the resultant of the driving force  $F = jB$ . The limiting diffusion current being proportional to the involved electron number, then eq 4 becomes

$$\alpha = k'nBC^* \quad (7)$$

and (5)

$$I_{\text{lim}} = k''n^{4/3}FD^{2/3}A^{5/6}C^{*4/3}B^{1/3} \quad (8)$$

This 4/3 value has been already argued by Aogaki<sup>19</sup> for the  $\text{Cu}^{2+}/\text{Cu}$  system.

Finally, we have introduced kinematic viscosity ( $k'' = K\nu^x$ )

$$I_{\text{lim}} = Kn^{4/3}FD^{2/3}A^{5/6}C^{*4/3}B^{1/3}\nu^x \quad (9)$$

Values of the  $K$  constant and  $x$  exponent were established empirically.

Solutions were 0.05 M in  $\text{Cu}^{2+}$ , and the electrolytic bath viscosity was changed by  $\text{H}_2\text{SO}_4$  and glycerol additions.

The first stage of work was to obtain the diffusion coefficient of  $\text{Cu}^{2+}$  in every electrolytic solution with a rotating electrode: limited diffusion current was measured for various angular rotation rates ( $\omega$ ) and  $D$  was determined using linear regression according to Levich's relationship (10)

$$I_{\text{lim}} = 0.62nFAD^{2/3}C^*\nu^{-1/6}\omega^{1/2} \quad (10)$$

The second stage was to transform eq 9 to obtain  $K\nu^x$  values with different magnetic inductions.

$$I_{\text{lim}}/(n^{4/3}FD^{2/3}A^{5/6}C^{*4/3}) = K\nu^x B^{1/3} \quad (11)$$

Results are given in Table 3.

It has to be noticed that for viscosity higher than  $2.8 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  the magnetically induced convection is too weak to get a linear relationship of the current versus  $B^{1/3}$ . This result has to be compared with those of ref 32 in which the normal component of the fluid velocity has to be taken into account.

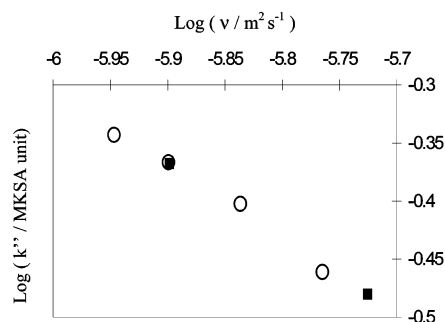
When the current was proportional to  $B$  to the power 1/3,  $\log(K\nu^x)$  was plotted versus  $\log \nu$  (Figure 9). A straight line was obtained with an  $r^2$  correlation coefficient of 0.993. The slope gives an  $x$  exponent from  $\nu$  equal to  $-0.645$ , therefore  $x = -2/3$ .

Then, the  $K$  value was calculated for each experiment with eq 9 and with  $x$  equal to  $-2/3$ . The  $K$  mean value obtained was equal to  $5.0 \times 10^{-5}$  in MKSA units.

Therefore relationship (11) becomes

$$I_{\text{lim}} = 5.0 \times 10^{-5}n^{4/3}FD^{2/3}A^{5/6}C^{*4/3}B^{1/3}\nu^{-2/3} \quad (12)$$

At last, we have recalculated the limiting current of Figure 2 (for that experiment, the electroactive species concentration is



**Figure 9.**  $k''$  value (eq 8) vs kinematic viscosity  $\nu$  for copper electrodeposition. Conditions: Cu electrode, diameter = 3 mm;  $[\text{CuSO}_4] = 0.05 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.9\text{--}1.8 \text{ mol L}^{-1}$ ;  $[\text{glycerol}] = 0\text{--}5.3 \text{ mol L}^{-1}$ ;  $T = 303 \text{ K}$ .

10 times higher than the one used for determination of relationship 12). In this case, the theoretical values obtained by relationship 12 are in good accordance with experimental results (Table 2).

We have to emphasize that considering the solution density  $\rho$  as a constant and using the Walden's relationship ( $D\eta = \text{constant}$ ), because the viscosity  $\eta = \rho\nu$ , we obtain  $D\nu = \text{constant}$ . Therefore, relationship 11 leads to a current proportional to  $D$  to the power 4/3 whereas the Leventis' relationship (6) leads to a current proportional to  $D$  to the power 5/4. Once more, the difference between these two exponents (1/12) is not significant.

## Conclusion

Until now, researches concerning magnetohydrodynamics have exhibited an influence of magnetic field on limiting current, and numerous works have dealt with relationships between the current and magnitude of the magnetic field and other physical or chemical properties. To increase knowledge on MHD effects upon electrochemical systems concerning industrial applications, we have conducted analyses on the copper electrodeposition in sulfuric acid.

First, we have shown it was possible to jam magnetoconvection, which offers new opportunities for studying other phenomena induced by a magnetic field (e.g., modifications of kinetics). Therefore results obtained with and without a magnetic field should be compared directly.

Moreover, we have proposed modifications for the MHD equation of limiting diffusion current versus magnetic field amplitude proposed by Aaboubi et al.<sup>22</sup> Kinematic viscosity and the number of involved electrons were taken into account. We analyzed the effects of those parameters and showed that the limiting current of the copper electrodeposition was proportional to the viscosity to the power  $-2/3$  and to the number of involved electrons to the power  $4/3$ . All these numerical values are valuable for copper electrodeposition from a sulfuric bath. Despite a different theoretical approach, Leventis' relationship

and ours exhibit very small differences. Consequently, further analyses and deeper theoretical investigations are needed to improve knowledge of the convective effects of a magnetic field upon electrochemical reactions.

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