

Magnetic Field Effects on Electrochemical Processes: A Theoretical Hydrodynamic Model

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The effect of a static homogeneous magnetic field that is directed parallel to the planar electrode surface is analyzed in terms of a hydrodynamic boundary layer formation and equivalent mass transfer model for a semi-infinite electrode. The model predicts the decrease of the boundary layer thickness upon increasing either the magnetic field strength, B , or reagent bulk concentration, C^* , with the power dependence corresponding to $C^{*4/3}B^{1/3}$. This permits the interpretation of the enhanced mass transfer at electrode surfaces via hydrodynamic principles.

Introduction

The study of magnetic field effects on electrochemical systems dates back more than 100 years with the research efforts of Faraday.¹ Currently, the term “magnetoelectrolysis” reflects the different modes by which magnetic fields influence the performance of electrochemical processes. The interest in the interactions of magnetic fields with electrochemical systems stems from the possibilities to control the morphology of products that are electrodeposited on the electrodes or to control the mass transport of reactive components at the electrode surface, thus controlling the reaction rate at the electrode/electrolyte interface.

Different types of forces may be exerted on electroactive species in a magnetic field, such as forces originating from the motion of charged species, forces resulting from magnetic field gradients, or paramagnetic species concentration gradients.² Such forces may contribute to field-driven transport phenomena and thereby influence the reactions at the electrode interfaces.³ It was suggested that the magnetic field effects on electrochemical processes originate from field-induced convection, where the different magnetic forces acting on the electroactive components result in the solution convection at the electrode surface.^{3b} The convection decreases the diffusion boundary layer thickness and thereby increases the mass transport at the electrode and the resulting limiting electrical current. The solution flow is generated by the momentum transfer from magnetic field-driven ions to neighboring solute molecules. Thus, the overall magnetic field effect on the dynamics of the system may be described as a *magnetic body force* that acts on a unit volume of solution element through which the current passes, rather than in terms of the microscopic interaction of the field with the discrete current generating ions. The analogy between magnetic fields and electrode rotation as a means of generating convection has been noted previously.^{4,5} The equivalence of the magnetic field effect with that of a rotating disk electrode supports the idea that the field acts to induce convection in the solution.

Substantial efforts were directed to relate the mass-transport limited current, I_L , with parameters that affect the electrochemical transformations in the systems studied under an externally imposed magnetic field. These efforts are based on the functional

fitting of the observable limiting currents with the different parameters used in the system. There is, however, no comprehensive theoretical model that quantitatively describes the relation between the resulting limiting currents, the externally applied fields and other parameters of the system. Most of the empirical fittings correlated the limiting current, I_L , with the strength of the magnetic field, B , $I_L \sim B^b$, and the reported value of b ranged between 0.25 and 1.6.^{6–9} For example, Aogaki et al.^{6a} reported that the I_L value in the electrodeposition of copper in a system consisting of two closely spaced parallel electrodes is proportional to $C^{*3/2}B^{1/2}$, where C^* is the bulk concentration of the redox-active species. In another study of Aogaki et al.,^{6b} where the same process was examined in a wide cell configuration, the limiting current was reported to be proportional to $C^{*4/3}B^{1/3}$. More recently, White and co-workers⁸ have reported on the magnetic field effects on the reduction of nitrobenzene or acetophenone in acetonitrile at microelectrodes. These studies led to the conclusion that the enhancement in the limiting current ($I_L - I_L^0$), where I_L and I_L^0 are the limiting currents in the presence and absence of a magnetic field, respectively, is proportional to the strength of the magnetic field. Another report of Aaboubi et al.,⁴ studying the ferricyanide–ferrocyanide electroactive couple, showed an empirical relation of the limiting current I_L being proportional to $C^*\alpha^{1/3}$, where α was defined as the magnetohydrodynamic velocity gradient, $\alpha = kBC^*$, and k is an empirical constant. In a later study of this group,⁷ the voltammetric responses of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ under an applied magnetic field at a microelectrode showed that steady-state limiting currents are proportional to $C^{*4/3}B^{1/3}$.

The dependence of I_L on different parameters under an applied magnetic field has been systematically studied by Leventis and co-workers,¹⁰ using a range of compounds and solvents selected according to their different diffusion coefficients and kinematic viscosities, respectively. For example, one of the studied redox compounds was N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD) in the presence of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. When the double logarithmic (log–log) plot method was applied, it was found that the limiting current could be expressed in terms of a simple power law, given by

$$I_L = (4.3 \times 10^3) n^{3/2} A^{3/4} D \nu^{-1/4} C^{*4/3} B^{1/3} \quad (1)$$

where ν is the viscosity of the solution, C^* and B correspond

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to the bulk concentration of the electroactive species and the strength of the magnetic field, respectively, D is the diffusion constant of the electroactive species, and A and n are the electrode surface area and the number of electrons per molecule participating in the electrochemical reaction, respectively.

An early attempt to model the magnetic field effect on the limiting current of electrochemical transformations was reported by Fahidy.^{3b} The fact that the Lorentz force acting on the charged electrolyte components yields a transverse flow of the solution parallel to the electrode surface allowed him to propose that the diffusion boundary layer thickness under an applied magnetic field, $\delta_D(B)$, is smaller than the diffusion boundary layer without a magnetic field, $\delta_D(0)$, eq 2, and accordingly, the enhancement in the limiting current is given by eq 3, where I_L and I_L^0 are the limiting currents in the presence and absence of a magnetic field.

$$\delta_D(B) = \delta_D(0) - \alpha_1 B^m \quad (2)$$

$$I_L(B) = I_L^0 + \alpha_2 B^l \quad (3)$$

Hinds and co-workers performed experiments on the electrochemical deposition of copper at different external magnetic fields.⁹ By fitting the experimental data for the limiting currents to eq 3, they derived the value of $l = 0.35$.⁹

Although some deviations exist, most of the experimental studies suggest that the limiting currents under an applied magnetic field relate to the concentration of the electroactive reactant and the magnetic field strength by the function $C^{*4/3}B^{1/3}$. Nonetheless, there is no comprehensive theoretical model that accounts for the magnetic field effects on electrochemical processes at electrode surfaces. Here we wish to formulate a theoretical paradigm that quantitatively accounts for the magnetoelectrolysis effect. The present paper will describe the detailed derivation of the theoretical model and its consistency with the experimental results.

Formulation of the Theoretical Model

We will regard the theoretical model for a planar semi-infinite electrode with the magnetic field applied parallel to the surface. The basic hydrodynamic equations governing mass transfer under a magnetic force are well-known. Yet, because of the nonlinear character of these equations and the fact that neither the velocity nor the concentration profile near the electrode are known a priori, rigorous analytical solutions cannot be obtained.^{3,10a} The evolution of the concentration profiles of the redox-active species is given by the continuity equation for that species, which in the absence of migration (i.e., in the presence of a large excess of supporting electrolyte) is given by solution of the convective–diffusion equation, eq 4¹¹

$$\partial C / \partial t = D \nabla^2 C - V \nabla C \quad (4)$$

where V is the fluid velocity, and D and C are the diffusion coefficient and the concentration of the electroactive species, respectively. Under stationary conditions in solution (no natural or forced convection), the diffusional material flux, j , involved per unit area and time is given by Fick's first law.

$$j = -D \nabla C \quad (5)$$

According to the Nernst approximation, a concentration gradient exists only in the diffusion boundary layer of thickness δ_D , while in the rest of the solution the concentration is equal to C^* and the flux of the redox-active species toward the

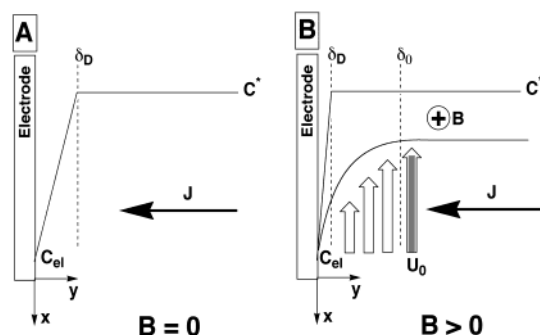


Figure 1. Schematic illustration of the mechanism of enhanced mass transport of a charged electroactive species under an applied magnetic field.

electrode is given by eq 6

$$j = D (C^* - C_{el}) / \delta_D \quad (6)$$

where C^* is the bulk and C_{el} is the surface concentration of electroactive species (reactant) at the electrode, respectively. For sufficiently high current densities, achieved upon application of an appropriate electrode potential, C_{el} tends to zero, since for mass-transport limited reactions the reaction rate at the electrode surface is substantially faster than the reactant supply. Therefore, the electrochemical boundary conditions for the mass-transport limited current could be written as

$$C = 0|_{y=0}; \quad C = C^*|_{y \rightarrow \infty} \quad (7)$$

where y notes the direction normal to the electrode surface.

The current produced by the redox reaction in the mass-transport limited regime is controlled by the diffusional flux of the electroactive species to the electrode surface (eq 6). This flux is directed orthogonal to the electrode surface and defines the direction of the net current involved in the Faradaic reaction. The limiting current as a result of the Faradaic process of the redox-active species, I_L , can be formulated as

$$I_L = nAFj|_{y=0} = ADnFC^* / \delta_D \quad (8)$$

where n is the number of electrons involved in the Faradaic process, A is the electrode surface area, and F is the Faraday constant.¹¹ The limiting current density is given by

$$i_L = |i_L| \hat{y} = \hat{y} (DnFC^* / \delta_D) \quad (9)$$

where \hat{y} is the unit vector in the direction normal to the electrode surface. As the electron transfer at the electrode surface requires charge compensation, a flow of ions is generated, and this flow is influenced by the external magnetic field.

In our model we will consider the effect of a homogeneous magnetic field that is directed parallel to the electrode surface. The magnetic body force, F_L , acting on the unit volume of charge-carrying ions is given by the Lorentz equation, eq 10, and corresponds to the vector product of the net current density, i_L , and the magnetic field strength, B .

$$F_L = i_L \times B \quad (10)$$

The Lorentz force exerted on the moving ions results in a momentum transfer to the solvent, and since the net current is directed normal to the electrode surface, the resulting flow of the solvent is tangential with respect to the electrode surface. This effect of the magnetic field on the passing current and thus generated fluid motion is schematically depicted in Figure 1.

While a diffusion boundary layer of thickness δ_D is formed due to the electrochemical process in the absence of the magnetic field, Figure 1A, the magnetic field yields a tangential solution flow that is perpendicular to the diffusion flux, and it is characterized by a hydrodynamic boundary layer of thickness δ_0 , Figure 1B.

In order to determine the concentration profile of the redox-active species near the electrode under conditions of electrochemically induced diffusion (according to eq 4) and generated magnetohydrodynamic flow, one has to determine the velocity profile, $V(x,y)$ of the species in the fluid. The velocity profile can be obtained by solving the forced Navier–Stokes equation (NSE), eq 11, and the continuity equation, eq 12¹²

$$\rho \left(\frac{\partial \vec{V}}{\partial t} + (\vec{V} + \nabla) \vec{V} \right) = -\nabla P + \eta \Delta \vec{V} + \vec{F}_i \quad (11)$$

$$\nabla \cdot \vec{V} = 0 \quad (12)$$

The Navier–Stokes equation expresses Newton's second law of motion for a unit volume of an incompressible Newtonian fluid of constant density, ρ , and dynamic viscosity, η . The left-hand side of the equation represents the acceleration of the fluid volume element, while the right-hand side is the sum of the total volume forces acting on it. The velocity vector of the unit volume element of fluid is denoted as V , and, assuming the steady flow, we obtain $\partial V/\partial t = 0$. The first term on the right-hand side is the force due to the hydrodynamic pressure gradient, ∇P , through the system and the second term $\eta \Delta V$, expresses the frictional forces between the unit volume element and the surrounding fluid. Momentum is transferred from faster moving layers of fluid to slower moving layers. The third term, F_i , refers to any external volume forces, acting on the fluid element. Evidently, eqs 11 and 12 that represent a hydrodynamic problem should be coupled to eq 4 via the concentration of the electroactive species near the electrode which is controlled by the electrochemical boundary conditions, eq 7.¹³ For the system under consideration the external volume force is the Lorentz force F_L , (eq 10), and it is coupled to the reactant concentration gradient via the net current density i_L (eq 9).

The flow velocity profiles for the systems considered here have been obtained by flow imaging using a special two-disk electrode system,^{10a,c} where the collection current of the auxiliary electrode mapped the main electrode surface as a function of the angle with respect to the direction of magnetic field B . The collection current, proportional to the flow velocity component in a given direction, was found to have a pronounced maximum at an angle equal to 90°, and thus the flow could be regarded as unidirectional. A similar result has been obtained by flow imaging with a scanning electrochemical microscope (SECM).^{8b} Thus, the generated flow has only one velocity component tangential to the surface and perpendicular to the magnetic field direction. Indeed, previous studies^{10c} have imaged the magnetic field effect on the fluid flow at the electrode.

The entire zone of fluid motion above the electrode may be roughly subdivided into two regions: a region of inviscid motion and a boundary layer region in which viscosity plays a crucial role. This region is known as the hydrodynamic (Prandtl) boundary layer, and its thickness, denoted as δ_0 , is given as¹⁴

$$\delta_0(x) \approx 5.2 (\nu X/U)^{1/2} \quad (13)$$

where X is the distance from the plate upstream edge, ν is the solvent viscosity, and U is the flow velocity. (It should be noted that eq 13 is applicable only for laminar flow.) Although the

hydrodynamic boundary layer occupies a small volume (a typical thickness in a liquid of viscosity $\nu = 10^{-2}$ cm²/s moving with velocity $U = 10$ cm/s is $\delta_0 = 0.1$ cm), its properties dominate the hydrodynamic behavior of the fluid flow.

According to the Nernst model, the fluid within the diffusion boundary layer, having thickness δ_D , is assumed to be quiescent, and the transport of electroactive species is accomplished by molecular diffusion. Upon application of the magnetic field, the Lorentz force induces a flow motion in the bulk solution at the surface, mainly tangential.^{5,10} This leads to the formation of a hydrodynamic boundary layer of thickness δ_0 , eq 13. The relationship between the thickness of the diffusion (Nernst) layer of the electroactive species, δ_D , and the thickness of hydrodynamic boundary layer of the fluid moving over the plate, δ_0 was derived by Levich¹⁴

$$\delta_D \approx 0.62 Pr^{-1/3} \delta_0 \quad (14)$$

where Pr is Prandtl number, $Pr = \nu/D$, a dimensionless parameter that characterizes the regime of convection. Thus for a Pr on the order of 10^3 , we obtain a value of δ_D that is about one-tenth δ_0 .

Chronoamperometric experiments have indicated that the magnetic field does not effect the diffusion coefficients of electroactive species.^{9,10} On the other hand, the magnetic field exerts a clear effect on the diffusion-limited current, which increases as the magnetic field is elevated. Since the diffusion coefficients remain constant under a magnetic field, this implies that the concentration gradient ∇C must increase in the presence of the magnetic field, according to eqs 6 and 8. Since the concentration gradient is approximated by $\nabla C = C^*/\delta_D$ this implies that the diffusion boundary layer thickness decreases in the presence of the magnetic field.

In the following section we formulate a simple quantitative model that describes the magnetic field effect on the mass transport of the electroactive species to the electrode and, as a result, the augmentation of the limiting current density. The model is developed using the boundary layer approximation for the forced NSE (eq 11). The incorporation of the Lorentz force as an external force into the NSE allows us to relate the bulk flow velocity to the magnetic body force acting on the solution in order to obtain the expression for δ_D as a function of applied magnetic field. We do not regard any other type of possible forces, since our model deals with a homogeneous magnetic field imposed on a nonmagnetic solution and a nonmagnetic electrode at a constant temperature. For a detailed review on the possible forces in the system the reader is referred to the paper of Hinds et al.⁹

We regard the unidirectional steady laminar flow, streaming parallel to the electrode surface inside the boundary layer; thus, $V = V_x(y)$, where x is directed along the surface (that means the flow velocity has only one component, V_x). To simplify the NSE within the boundary layer, we can utilize the fact that the thickness of this layer is very small compared to its length along the body ($L \gg \delta_0$). In viscous flow all velocity components must become zero at the surface of a solid body immersed in a fluid. This is known as the “no slip” condition $V|_{y=0} = 0$, which along with $V|_{y=\infty} = U_0$ at the outer edge comprise boundary conditions for the hydrodynamic flow in the boundary layer.¹² Hence, there is a region immediately adjacent to the solid surface where the unidirectional flow velocity, V_x , changes rapidly from zero to its value in the bulk stream, U_0 , in the direction perpendicular to the electrode surface (y -direction), while its tangential rate of change is comparatively small.

In the boundary layer approximation the pressure does not change in the direction normal to the surface, but it remains equal to the pressure outside the boundary layer thus $\partial P/\partial y = 0$.^{12,14} On the outer edge of the boundary layer the fluid velocity is constant and equal to U_0 ; hence, from the Bernoulli equation it follows that the pressure in the outer region is also constant. As a result, the term containing the pressure gradient in eq 11 can be omitted. Under these conjectures the forced steady Navier–Stokes equation for unidirectional laminar flow within the boundary layer can be simplified as follows (for the detailed derivation of the relation see the Appendix):

$$\rho V_x \frac{\partial V_x}{\partial x} = \eta \left(\frac{\partial^2 V_x}{\partial y^2} \right) + F_L \quad (15)$$

The term $\eta \partial^2 V_x / \partial y^2$ could be determined using a further consideration: within the boundary layer, viscous shear between the fluid flow and the electrode causes the fluid velocity to become zero at the electrode surface. Thus, all changes in tangential fluid velocity from U_0 to the zero value occur over δ_0 ; therefore, the term $\eta \Delta v$ can be rewritten approximately as $\eta U_0 / \delta_0^2$. Our choice of δ_0 as the characteristic length in the system and U_0 as the *characteristic velocity* is equivalent to stating that the dominant dissipation of the energy input into the system is the shear between the fluid flow and the electrode plate. This dissipation is balanced against the external force, F_L , or the driving term, which could lead to the setup of the fluid motion over the electrode surface. To produce the flow, the driving force, F_L , proportional to $i_L B$, should overcome the dissipative force term $\eta U_0 / \delta_0^2$. We will write the Lorentz force as $F_L = DBnFC^*/\delta_D$ (using eqs 10 and 9) and then will equalize the two terms to obtain the further relation

$$\frac{U_0}{\delta_0^2} \approx \frac{nFC^*DB}{\delta_D} \quad (16)$$

Thus, after substituting proper characteristic values and using the relation between δ_0 and δ_D (eq 14, $\delta_D \approx 0.62 Pr^{-1/3} \delta_0$), we obtain the following expression for the generated flow velocity U_0 :

$$U_0 \approx \frac{W\delta_0}{0.62} \quad (17)$$

where $W = nFC^*DBPr^{1/3}\eta^{-1}$.

Then we substitute the derived velocity U_0 into the expression for the hydrodynamic boundary layer thickness δ_0 (eq 13, $\delta_0 \approx 5.2 (\nu X/U)^{1/2}$, where the distance X is assumed to be $X = R$, R – electrode radius), thus excluding U_0 , and we obtain the final expression for δ_0 that can be written in the form

$$\delta_0 \approx 2.56 (\nu R/W)^{-1/3} \quad (18)$$

Therefore, the diffusion boundary layer thickness (using eq 14, $\delta_D \approx 0.62 Pr^{-1/3} \delta_0$) can be expressed as

$$\delta_D \approx 0.62 Pr^{-1/3} \delta_0 \approx 1.59 (\rho R \nu^{2/3} D^{1/3})^{1/3} (nFC^*B)^{-1/3} \quad (19)$$

The latter expression, eq 19, provides the dependence of δ_D on the parameters controlling the magnetoelectrolysis. Thus, the mass-transport coefficient $m = D/\delta_D$ is therefore

$$m \approx 0.63(\rho R)^{-1/3} \nu^{-2/9} D^{8/9} (nFC^*B)^{1/3} \quad (20)$$

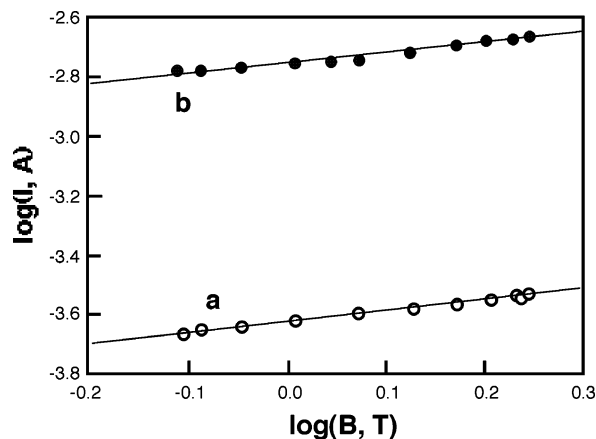


Figure 2. Effect of the magnetic field strength on the limiting currents in two TMPD solutions (50.00 and 10.375 mM, respectively) consisting of $\text{CH}_3\text{CN}/0.5 \text{ M TBAP}$. Double logarithmic plots for collection currents: (a) $[\text{TMPD}] = 10.375 \text{ mM}$, slope = 0.36; (b) $[\text{TMPD}] = 50.00 \text{ mM}$, slope = 0.44. (Adopted from ref 10a, Figure 11b. Reprinted with permission from ref 10a. Copyright 1998 American Chemical Society.)

This implies that the limiting current density, i_L , could be written as

$$i_L \approx nFmC^* \approx 0.63(\rho R)^{-1/3} D^{8/9} \nu^{-2/9} (nFC^*)^{4/3} B^{1/3} \quad (21)$$

and therefore the limiting current, I_L , for a disk electrode ($A = \pi R^2$) could be written as

$$\begin{aligned} I_L &\approx AnFmC^* \approx 0.63\pi^{1/6} A^{5/6} \rho^{-1/3} D^{8/9} \nu^{-2/9} (nFC^*)^{4/3} B^{1/3} \\ &\approx KA^{5/6} D^{8/9} \nu^{-2/9} (nC^*)^{4/3} B^{1/3} \end{aligned} \quad (22)$$

where $K = 0.63\pi^{1/6} F^{4/3} \rho^{-1/3}$ or $K \approx 4 \times 10^6$ for $\rho \approx 1$. It should be noted that the derived power dependence of $n^{4/3}$ is consistent with the derived powers of $C^{*4/3}$ and $F^{4/3}$, as follows from eqs 10 and 19. The expression nFC^* represents the value of the charge transferred by a unit volume of the solution upon electrochemical reaction. Hence, the body force acting on a unit volume of the solution (eq 10) and, accordingly, δ_D and the resulting i_L should be proportional to the n , F , and C in the same power, as was shown.¹⁵

Analysis of Experimental Results by the Theoretical Model

The formulated model implies that the limiting current under an applied magnetic field relates to the different system parameters in the form of a simple power dependence (eq 22). Most importantly, it should be realized that the coupling of the electrogenerated diffusion boundary layer to the hydrodynamic flow, induced by the magnetic field, leads to the $C^{*4/3}B^{1/3}$ power dependence of the limiting current. We will now demonstrate the validity of this model with some experimental results, discuss some experimental deviations from the model, and analyze raw experimental data in terms of the formulated model.

In Figures 2 and 3 we show the results obtained by Leventis et al., that correspond to the oxidation of TMPD.^{10a} Figure 2 shows the double logarithmic plot of the generated limiting currents, I_L , obtained at two different concentrations of TMPD (50.00 mM and 10.375 mM), by varying the strength of applied magnetic fields, B , as expected from the formulated model. Clearly, two parallel lines are observed with a slope that corresponds to $1/3$. Figure 3 shows the double logarithmic plot of the limiting current value observed by varying the concentra-

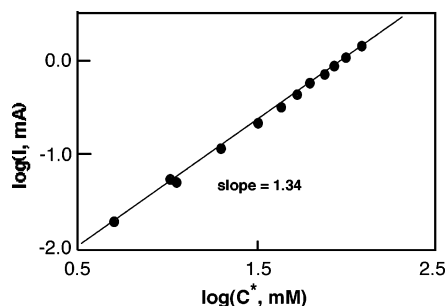


Figure 3. Effect of the concentration on the limiting currents observed upon electrochemical oxidation of TMPD in $\text{CH}_3\text{CN}/0.5 \text{ M TBAP}$ under an applied magnetic field of $B = 1.75 \text{ T}$. Double logarithmic plot for the limiting current. (Adopted from ref 10a, Figure 2 inset b. Reprinted with permission from ref 10a. Copyright 1998 American Chemical Society.)

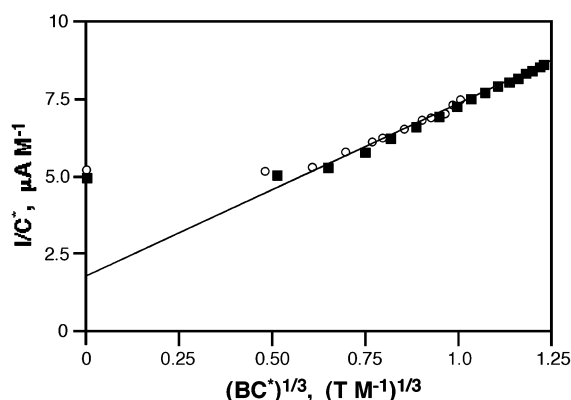


Figure 4. Normalized cathodic limiting currents I_L/C^* vs $(BC^*)^{1/3}$ obtained for different concentrations C^* of $\text{Fe}(\text{CN})_6^{3-}$ ions: (■) = 1.0 M and (○) = 0.75 M. (Adopted from ref 7b, Figure 3. Reprinted with permission from ref 7b. Copyright 2003 Electrochemical Society.)

tion of TMPD under a constant applied magnetic field of 1.75 T. Clearly, a linear relation is observed with a slope that corresponds to 1.34, that is close to the value of $4/3$ as predicted by the formulated model, eq 22. In Figure 4 we show the results reported by Aaboubi et al.,^{7b} that correspond to the reduction of $\text{Fe}(\text{CN})_6^{3-}$ at two different concentrations (1 and 0.75 M) in the presence of imposed magnetic fields. In this plot the experimental results are presented as described in the original report. Clearly, the theoretically predicted linear relation between I_L and $B^{1/3}C^{4/3}$ is observed with a small deviation in the range of the weak magnetic field and originating from natural convection.⁷ In Figure 5, we present values of the normalized limiting current density, i/i_0 , where i_0 is the current density for $B = 0$, that were extracted from the voltammetric responses corresponding to the reduction of copper,⁹ curve a, and to the electrochemical deposition of nitrobenzene,⁵ curve b, at different external magnetic fields. On a double logarithmic plot curve a yields the theoretically predicted slope of 0.33, while for curve b, we obtained a slightly lower slope than expected from our model, that corresponds to 0.24. Furthermore, we would like to emphasize that our model predicts also the power dependence on n^k , D^d , and ν^b . Experimental values obtained by Leventis for these parameters ($k = 3/2$, $d = 1$, and $b = -1/4$) are very close to the predicted values ($k = 4/3$, $d = 8/9$, and $b = -2/9$).^{10a}

Conclusions

The present study has formulated a quantitative theoretical model that accounts for the homogeneous magnetic field effect on electrochemical reactions at planar semi-infinite electrode

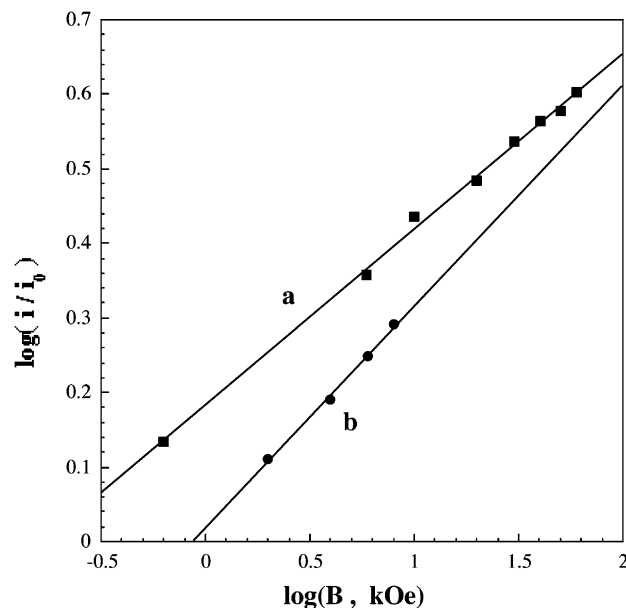


Figure 5. Replotted data of normalized limiting currents as a function of the magnetic field strength for (a) electrochemical reduction of 2.0 M of nitrobenzene (NB) in acetonitrile (CH_3CN) solution that includes 0.2 M $[n\text{-Bu}_4\text{N}]\text{PF}_6$ as electrolyte (adopted from ref 9, Figure 2. Reprinted with permission from ref 9. Copyright 2001 American Chemical Society); (b) the cathodic currents at a copper working electrode upon electrodeposition of copper from a 0.75 M CuSO_4 solution at pH = 0.5, applied potential -0.5 V vs Ag/AgCl (adopted from ref 5, Figure 2. Reprinted with permission from ref 5. Copyright 1997 Elsevier).

surfaces, with the field parallel to the surface. The model is based on the boundary layer approximation of the NSE associated to the Nernst layer approximation. The cornerstone of the model is the relation between the thickness of the diffusion boundary layer, δ_D , and the thickness of hydrodynamic boundary layer, δ_0 , obtained by Levich.¹⁴ Basically, we coupled the thickness of the diffusion boundary layer, resulting from the electrochemical process, with the hydrodynamic flow of the solution at the electrode interface induced by the magnetic field, as a result of the Lorentz force. By comparing the dissipative shear force term in the forced NSE with the Lorentz force, F_L , we derived the expression for the velocity of the generated fluid flow (eq 17). The developed model predicts that the diffusional layer thickness, δ_D , is proportional to $(nC^*B)^{-1/3}$. The shrinkage of the diffusion boundary layer enhances the supply of the electroactive reactant to the electrode and results in the enhanced limiting currents in the presence of the applied magnetic field. Our theoretical model implies that the mass-transport coefficient m is proportional to $B^{1/3}$ and the limiting current is proportional to $(nC^*)^{4/3}B^{1/3}$, and it was successfully applied to the analysis of several experimental reports.

Several remarks should be made regarding the derived theoretical model and its anticipated significance: (i) In order to obtain a magnetic field effect on the electrochemical process, the net current associated with the electroactive species should pass through the system, and the effect is controlled by coupling of the net current to the imposed magnetic field. (ii) We suggest that the formulated theoretical model not only provides a solid background for the understanding of electrochemical transformations enhanced by means of an external magnetic field, but also could provide an insight into the enhancement of electrocatalytic and bioelectrocatalytic transformations and processes in fuel and biofuel cells, caused by means of an applied magnetic field.¹⁶

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Appendix: Derivation of Equation 15 from the Forced Navier–Stokes Equation

The forced Navier–Stokes equation and continuity equation could be written in a component form as

$$\rho \left(\frac{\partial V_i}{\partial t} + V_k \frac{\partial V_i}{\partial x_k} \right) = -\frac{\partial P}{\partial x_i} + \eta \frac{\partial^2 V_i}{\partial x_k^2} + F_i \quad (\text{A1-1})$$

$$\frac{\partial V_i}{\partial x_i} = 0 \quad (\text{A1-2})$$

where the summation has to be taken over subscripts which appear twice (here i, k has values x, y, z).

Let us consider the steady laminar two-dimensional flow of fluid choosing the y -axis perpendicular to the surface of the electrode and the x -axis along the surface. Taking into account the directions of a net current i and a magnetic field B (normal and tangential to the surface, correspondingly), we can conclude that the generated fluid stream velocity V is directed together with the Lorentz force F_L along axis x , thus $F_L = F_{Lx}$. Now the equations of motion for the velocity components in this steady unidirectional flow ($V = V_x(y)$) could be presented in the following reduced form (given that $V_y = 0$ and $F_L = F_{Lx}$):

$$\rho V_x \frac{\partial V_x}{\partial x} = -\frac{\partial P}{\partial x_i} + \eta \frac{\partial^2 V_x}{\partial x^2} + \eta \frac{\partial^2 V_x}{\partial y^2} + F_{Lx} \quad (\text{A2-1})$$

$$\frac{\partial V_x}{\partial x} = 0 \quad (\text{A2-2})$$

The entire zone of the fluid motion may be roughly subdivided into two regions: a region of inviscid motion and a boundary layer region in which viscosity plays an important role. If we designate the thickness of the boundary layer δ_0 , the dimension of the plate L and the flow velocity outside the boundary layer as U_0 , it may be assumed that the change in velocity V_x along the y -axis takes place over distances of the order of δ_0 , and along the x -axis over distances of the order of L .¹² The equations for flow could be expressed in dimensionless form by employing characteristic length and velocity factors. Let choose L , δ_0 , and U_0 as these factors, therefore $X_i = x_i/L$ and $Y_i = y_i/\delta_0$, $U_i = V_i/U_0$. These new coordinates X , Y lie between the limits of 0,1. With new variables eq 2-1 will take the following form

$$\rho \frac{V_x}{L} \frac{\partial V_x}{\partial X} = -\frac{1}{L} \frac{\partial P}{\partial X} + \frac{\eta}{L^2} \frac{\partial^2 V_x}{\partial X^2} + \frac{\eta}{\delta_0^2} \frac{\partial^2 V_x}{\partial Y^2} + F_{Lx} \quad (\text{A2-1}')$$

To simplify this equation within the boundary layer, we can utilize the fact that the thickness of this layer is very small compared to its length along the body. We will note that since $L \gg \delta_0$, then in the boundary layer

$$\frac{\eta}{L^2} V_x \ll \frac{\eta}{\delta_0^2} V_x \quad (\text{A3})$$

Therefore we can disregard the second term from the right-hand side of eq A2-1'.

The pressure does not change in the direction normal to the surface but remains equal to the pressure outside the boundary

layer, $\partial P/\partial y = 0$. On the outer edge of the boundary layer the fluid velocity is constant and equal to U_0 . From the Bernoulli equation it follows that the pressure in the outer region is also constant. As a result the term containing the pressure gradient in eq A3 can be omitted. Thus, the final form of the simplified NSE will look as

$$\rho \frac{V_x}{L} \frac{\partial V_x}{\partial X} = \frac{\eta}{\delta_0^2} \frac{\partial^2 V_x}{\partial Y^2} + F_{Lx} \quad (\text{A4})$$

Knowing that all terms in eq A4 are of the same order of magnitude, we can estimate the thickness of the boundary layer in the absence of an external force ($F_{Lx} = 0$) from eq A5:

$$\frac{V_x}{L} \frac{\partial V_x}{\partial X} \sim \frac{\nu}{\delta_0^2} \frac{\partial^2 V_x}{\partial Y^2} F_{Lx} \quad (\text{A5})$$

or evaluate the driving force value necessary to surmount the dissipation and set the flow into motion

$$\frac{\eta}{\delta_0^2} \frac{\partial^2 V_x}{\partial Y^2} = F_{Lx} \quad (\text{A6})$$

The velocity V_x at the outer edge of the boundary layer attains the value U_0 ; then from eq A6 we get

$$\eta \frac{U_0}{\delta_0^2} \sim \frac{nFDBC^*}{\delta_D} \quad (\text{A7})$$

Definition of Symbols Used in the Paper

- B = magnitude of the imposed magnetic flux density (T, tesla)
- C^* = bulk electroactive species concentration (M)
- I_L = magnitude of the limiting current under applied magnetic field (A)
- I_L^0 = magnitude of the limiting current without magnetic field (A)
- i_L = magnitude of the limiting current density under applied magnetic field (A m⁻²)
- A = area of the electrode (m²)
- j = diffusion flux of the electroactive species (mol s⁻¹ m⁻²)
- J = charge flux of the electroactive species (A m⁻²)
- D = electrolyte diffusivity (m² s⁻¹)
- F = Faraday's number (96 487 C equiv⁻¹)
- n = number of the electrons involved in the Faradaic process
- δ = boundary layer thickness (m)
- ν = kinematic viscosity (m² s⁻¹)
- η = dynamic viscosity (kg m⁻¹ s⁻¹)
- P = hydrostatic pressure (N m⁻²)
- ρ = fluid specific density (kg m⁻³)
- U_0 = bulk flow velocity (m s⁻¹)
- Pr = Prandtl number (D/ν)

References and Notes

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- (13) This is in contrast to the hydrodynamic problem of the rotating disk electrode, which has been solved for the velocity profile independently

of the electrochemical one.¹⁴ Obtaining the velocity profiles generated by a magnetic field is a much more complicated task, and an analytical solution analogous to the Levich equation for the rotating disk electrode still does not exist.

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(15) In a previous theoretical study (ref 6a) the power dependence of limiting current changes on the number of electrons associated with the electrochemical process was suggested to be $n^{3/2}$ in contrast to the present formulation that predicts $n^{4/3}$. This might originate from the fact that the present model uses the simplified boundary layer approximation whereas the model formulated in ref 6a uses the creeping flow approximation (fluid inertia terms are neglected).¹² Also, the geometrical configuration of the electrodes differs in the two models: while the present study uses the semi-infinite planar electrode geometry, the model in ref 6a utilizes a finite-size electrode configuration.

(16) For some recent reports describing magnetic field effects on fuel cell see: (a) Leddy, J.; Chung, H. In *39th Power Sources Proceedings* **2000**, 144. (b) Okada, T.; Wakayama, N. I.; Wang, L. B.; Shingu, H.; Okano, J.; Ozawa, T. *Electrochim. Acta* **2003**, *48*, 53. These systems, however, have no relation to the theoretical model described in the present paper.