

Magnetoconvection Phenomena: A Mechanism for Influence of Magnetic Fields on Electrochemical Processes

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The objective of this study is to suggest an interaction mechanism for the influence of static magnetic fields on electrochemical processes occurring at a ferromagnetic electrode immersed in a paramagnetic electrolytic solution. The hypothesis is that the magnetic field will cause a transport of all ions due to the difference in the magnetic susceptibility in the solution at the electrode surface. The ion transport induced by the magnetic field is directed from electrode into solution. Experimentally, the effects of static magnetic fields on electrochemical systems were observed only within systems consisting of ferromagnetic electrodes immersed in paramagnetic solutions. The results showed that the magnetic field caused an anodic polarization for the ferric/ferrous system and a cathodic polarization for the nickel/nickel-ion and the cobalt/cobalt-ion system. The results were obtained by the open-circuit potential and the potentiostatic/galvanostatic methods. The suggested interaction mechanism is magnetoconvection, which predicts that to obtain any magnetic field effect, there has to exist a gradient of paramagnetic ion concentration in the solution at the electrode surface. Theoretically, it is shown that the magnetic field tends to cause an additional convective transfer of all components of the solution, which will be generated in the vicinity of the electrode surface. Further, both the experimental results and the suggested mechanism show that the magnetic field effect increases with increasing magnetic flux density and magnetic susceptibility of the solution and decreases with increasing temperature and stirring rate. The evidence presented here show that the proposed hypothesis and the proposed interaction mechanism are verified.

Introduction

We suggest an interaction mechanism for the influence of static magnetic fields on electrochemical processes occurring at a ferromagnetic electrode immersed in a paramagnetic electrolytic solution.

Numerous studies concerning possible effects of static magnetic fields on electrochemical systems have been published, and several potential interaction mechanisms have been proposed. There are three established mechanisms through which static magnetic fields interact with chemical systems.^{1,2} They can be characterized as magnetomechanic, magnetohydrodynamic, and electronic interaction in nature. The magnetohydrodynamic mechanism originates through the interaction of magnetic fields with electrolyte flows leading to the induction of electrical potentials and currents. Examples are interaction of magnetic fields with electrochemical systems consisting of iron electrodes in copper sulfate solutions,³ and copper electrodes in copper sulfate solutions.^{4–10} The electronic interaction mechanism involves electron transfer via radical pair intermediates that are highly sensitive to static magnetic interactions. An

example is the photoinduced charge-transfer reaction that occurs in the bacterial photosynthesis.^{11–13} The magnetomechanical mechanism includes the orientation of magnetically anisotropic macromolecules in strong homogeneous fields and the translation of paramagnetic species in high gradient fields.^{1,2} Examples are the reduction of paramagnetic metal ions or metal oxides to ferromagnetic metal, which seems to be favorable within magnetic fields.^{14–19}

In some previous publications carried out by Waskaas,^{20–24} O'Brien and Santhanam,²⁵ and Ragsdale et al.,²⁶ the effects of magnetic fields on electrochemical systems have been explained in terms of a gradient of paramagnetic ions in the vicinity of an electrode surface, i.e., in terms of magnetoconvection, which is a kind of the magnetomechanical mechanism. However, their considerations were concentrated on transport of only paramagnetic ions because of the magnetic field.

The hypothesis is that the magnetic field will cause a transport of all ions because of the difference in the magnetic susceptibility in the solution at the electrode surface. The magnetic driving force applied to a liquid has the same direction as the gradient of paramagnetic ions. Since the gradient increases with distance from the electrode surface, the driving force has direction from the surface to the bulk of the solution. The same is valid for the velocity of the ions. As a secondary effect, the rates of the electrochemical reactions occurring at the electrode surface will tend to either increase or decrease.

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† Tragically, Prof. Yurij I. Kharkats died recently. I dedicate this manuscript to the memory of Prof. Kharkats, who carried out the theoretical part of the manuscript. I will always remember him as a warm person and for his brilliant mathematical solutions.

TABLE 1: Electrode Materials Used and Their Qualities, Purities, and Magnetic Properties^a

electrode material	quality and purity	magnetic property
iron	St 1203, DIN 1623. 99% Fe, 0.17% C, 0.2–0.5% Mn, traces of Si, P, and S	ferromagnetic
nickel	Falconbridge electrolytical nickel, 99.9% Ni	ferromagnetic
cobalt	Falconbridge electrolytical cobalt, 99.9% Co	ferromagnetic
manganese	MCFE Mn. 81.2% Mn, 17% Fe, 0.95% C, 0.27% Si	paramagnetic
chromium	SANICRO 28. 26.64% Cr, 30.6% Ni, 36.1% Fe, 3.3% Mo	paramagnetic
copper	KPT 42004, 99.98% Cu	diamagnetic
zinc	KPT 42005, 99.98% Zn	diamagnetic
stainless steel	KPT 64344, 74% Fe, 18% Cr, 8% Ni	paramagnetic

^a The reference electrode used was a standard calomel electrode.

TABLE 2: Solutions Used and Their Concentrations, pH, and Magnetic Properties

solution	concn [M]	pH	magnetic property
iron(III) chloride	0.1	1.81	paramagnetic
iron(III) chloride	0.4	1.31	paramagnetic
iron(III) chloride	1.0	0.85	paramagnetic
iron(III) chloride	1.5	0.56	paramagnetic
iron(III) chloride	2.0	0.33	paramagnetic
iron(II) chloride	1.0	1.91	diamagnetic
iron(III) sulfate	0.5	0.86	paramagnetic
iron(III) sulfate	1.0	0.35	paramagnetic
nickel(II) chloride	1.0	3.84	paramagnetic
nickel(II) sulfate	1.0	2.77	paramagnetic
cobalt chloride	1.0	4.57	paramagnetic
cobalt sulfate	1.0	6.47	paramagnetic
manganese chloride	1.0	6.81	paramagnetic
manganese sulfate	1.0	2.74	paramagnetic
chromium(III) sulfate	1.0	0.21	paramagnetic
copper chloride	1.0	2.57	paramagnetic
copper sulfate	1.0	3.33	paramagnetic
zinc chloride	1.0	4.98	diamagnetic
zinc sulfate	1.0	4.98	diamagnetic
magnesium chloride	1.0	4.62	diamagnetic
iron(II) chloride ^a	1.0	1.50	diamagnetic
iron(III) chloride ^a	1.0	0.72	paramagnetic
iron(III) sulfate ^a	1.0	0.82	paramagnetic

^a The temperature was 50 °C.

The purpose of this paper is to study experimentally the electrochemical processes occurring at the electrode surface under influence of the magnetic fields, to develop a mathematical model that describes the interaction mechanism for the magnetic field effect, to analyze the experimental findings in view of the developed model, and to argue in favor of the proposed hypothesis.

Experimental Section

In this section, the results of previous and recent experiments concerning possible effects of static magnetic fields on electrochemical reactions are given.

In both experimental methods used in this study, the exposure chamber was placed in the gap of an electromagnet. The exposure chamber consisted of an electrode immersed in a solution. The magnetic field was introduced horizontally and perpendicularly to the electrodes. The apparatus and procedure has been described in detail elsewhere.^{20,21}

The exposed electrodes used were made of materials of given qualities and different magnetic properties and are given in Table 1. Concerning the solutions, both solutions of one or two salts were used. They are given in Tables 2 and 3.

For all solutions, pH measurements were carried out by a standard pH meter (Radiometer PHM 62) and a combined pH glass electrode. The pH meter has automatic temperature compensation. The calibration was carried out according to standard procedure for two buffers at pH = 7.00 and 4.00. The measurements were done at 19.7 ± 0.5 °C.

TABLE 3: Mixed Solutions Used, Including Their Concentrations, pH, and Magnetic Properties

solution 1	concn [M]	solution 2	concn [M]	pH
iron(III) chloride	1.0	iron(II) chloride	0.5	0.99
iron(III) chloride	1.0	iron(II) chloride	1.0	0.57
iron(III) sulfate	0.5	magnesium sulfate	0.5	0.64
iron(III) sulfate	0.5	magnesium sulfate	1.0	0.58
iron(III) sulfate	1.0	magnesium sulfate	0.5	0.28
iron(III) sulfate	1.0	magnesium sulfate	1.0	0.16

Results from the previous experiments^{20–22} clearly show that the effect of static magnetic fields on electrochemical systems was observed only in systems consisting of ferromagnetic electrodes immersed in paramagnetic solutions. The results obtained by the open-circuit potential method showed a change in the potential of the ferromagnetic electrode (SCE) when the electrode was exposed to the magnetic fields. The observed magnetic field effect increased with increasing magnetic flux density and electrolyte concentration and decreased with increasing temperature and when the paramagnetic solutions were mixed with diamagnetic solutions. The results obtained by the potentiostatic/galvanostatic method showed that the magnetic field caused a change in the anodic and cathodic polarization of the ferromagnetic electrode. However, the magnetic field effect depended on the initial conditions of the electrode polarization. The magnetic field effect was found to increase with increasing magnetic flux density and electrolyte concentration and to decrease with increasing stirring rate. However, of particular interest are the changes in the open-circuit potential due to the external magnetic fields for electrodes and solutions of different magnetic properties, which are given in Table 4 and Figure 1, and the changes in the polarization curves, given in Figure 2.

Results from experiments concerning the open-circuit potential and possible changes in this potential due to external magnetic fields for iron electrodes and mixed solutions of different magnetic properties are given in Table 5. The measured changes in the open-circuit potentials (SCE) of electrodes made of iron (A), nickel (B), and cobalt immersed in solutions of 1 M iron(III) sulfate, 1 M nickel sulfate, and 1 M cobalt sulfate solutions due to the magnetic field are shown in Figure 3. The change in the potential for the iron/iron(III) sulfate system goes in the positive direction. For the other systems, the change is in the negative direction.

Figure 4 shows the anodic and cathodic polarization curves with and without a 800 mT magnetic field for a working electrode made of iron immersed in a 1 M iron(III) sulfate solution.

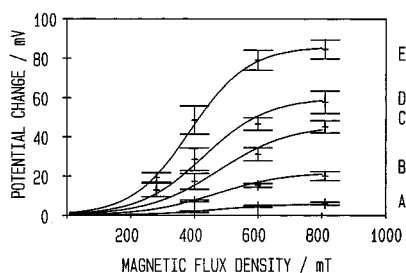
In Table 6 the effect of a 800 mT magnetic field on the electrode current through an iron electrode immersed in a buffered iron(III) sulfate solution at different electrode potentials is shown.

Results from experiments concerning possible induction effects are given in Table 7, which shows changes in the

TABLE 4: Open-Circuit Potentials (SCE) and Potential Changes Due to the Magnetic Field 800 mT for Different Electrodes in Different Solutions^a

electrode	solution	without <i>B</i> field (SCE) [mV]	with <i>B</i> field (SCE) [mV]	difference [mV]
iron	iron(III) chloride	-421	-376	45
iron	iron(III) sulfate	-439	-397	42
iron	nickel chloride	-636	-635	1
iron	nickel sulfate	-521	-523	-2
iron	manganese(II) sulfate	-713	-716	-3
iron	copper(II) sulfate	-83	-76	7
iron	iron(II) chloride	-530	-530	0
iron	iron(II) sulfate	-738	-738	0
iron	magnesium chloride	-980	-980	0
iron	zinc chloride	-635	-635	0
iron	distilled water	-451	-451	0
nickel	nickel chloride	-414	-425	-11
nickel	nickel sulfate	-378	-393	-15
cobalt	cobalt(II) chloride	-541	-543	-2
cobalt	cobalt(II) sulfate	-551	-570	-19
cobalt	nickel sulfate	-497	-500	-3
cobalt	manganese(II) sulfate	-499	-534	-35
cobalt	copper(II) sulfate	-188	-171	17
stainless steel	iron(III) chloride	-6	-6	0
manganese	manganese chloride	-965	-965	0
manganese	manganese(II) sulfate	-1038	-1038	0
chromium	chromium(III) sulfate	-130	-130	0
copper	copper chloride	-7	-7	0
copper	copper sulfate	-21	-21	0
copper	iron(III) chloride	-24	-24	0
zinc	zinc chloride	-1073	-1073	0
zinc	zinc sulfate	-1102	-1102	0
zinc	iron(III) chloride	-995	-995	0
iron ^b	iron(II) chloride	-617	-617	0
iron ^b	iron(III) chloride	-508	-475	33
iron ^b	iron(III) sulfate	-546	-525	21

^a The ion concentrations were 1 M. ^b The temperature was 50 °C.

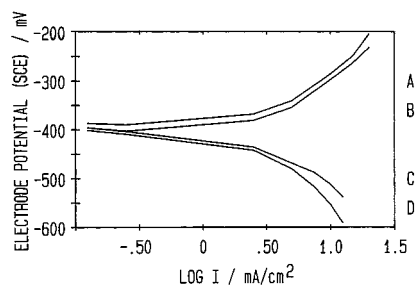
**Figure 1.** Measured change in the potential of the iron electrode (SCE) as a function of the magnetic flux density. The electrolyte was iron(III) chloride at concentrations (A) 0.1 M, (B) 0.4 M, (C) 1.0 M, (D) 1.5 M, and (E) 2.0 M. There was no stirring.

electrode potential when exposed to 300 mT magnetic fields with different rise times.

Theoretical

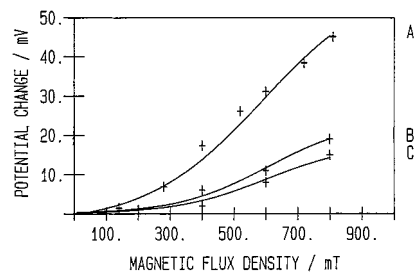
In this section, a theory for the observed magnetic field effect is developed. The aim of this theoretical development is to show in detail that the magnetic field will cause a transport of all ions because of the difference in the magnetic susceptibility in the solution at the electrode surface. This is a further development of the previous discussions carried out Waskaas,^{20–24} O'Brien and Santhanam,²⁵ and Ragsdale et al.,²⁶ which were concentrated on transport of only the paramagnetic ions due to the magnetic field.

The mathematical model is based on the Navier–Stokes equation for the description of solution flow, Nernst–Planck's equation for the description of electrodifusion in the solution

**Figure 2.** Measured anodic and cathodic polarization curves for two different working electrodes with (A and C) and without (B and D) exposure to an 800 mT magnetic field. The working electrodes were made of iron, the electrolyte was 1 M iron(III) chloride, and the stirring rate was 120 revolutions/min.**TABLE 5: Open-Circuit Potential (SCE) and Possible Changes in This Potential Due to Magnetic Fields (800 mT) for Iron Electrodes in Different Mixed Solutions^a**

electrode	solution	without <i>B</i> field (SCE) [mV]	with <i>B</i> field (SCE) [mV]	difference [mV] (SCE)
iron	1 M iron(III) chloride			
	0.5 M iron(II) chloride	-452	-433	19
iron	1 M iron(III) chloride			
	1 M iron(II) chloride	-431	-416	15
iron	1 M iron(III) sulfate			
	0.5 M magnesium sulfate	-403	-384	19
iron	1 M iron(III) sulfate			
	1 M magnesium sulfate	-405	-391	14
iron	0.5 M iron(III) sulfate			
	0.5 M magnesium sulfate	-566	-554	12
iron	0.5 M iron(III) sulfate			
	1 M magnesium sulfate	-553	-546	7

^a The concentrations for both solutions are given.

**Figure 3.** Measured change in the open-circuit potentials (SCE) of electrodes made of iron (A), nickel (B), and cobalt (C) immersed in solutions of 1 M iron(III) sulfate, 1 M nickel sulfate, and 1 M cobalt sulfate solutions as a function of magnetic flux density. The stirring rate was 120 revolutions/min. The electrode potential for iron/iron(III) sulfate system becomes more positive. The other systems become more negative.

at the electrode surface, the condition of local electroneutrality of solution as a simplified form of Poisson equation, and finally, the density of energy of a magnetic field.

The density of energy of the magnetic field in solution can be written in the form²⁷

$$W_s = \frac{1}{2} \mu_0 (1 + \kappa_s) H_s^2 \quad (1)$$

With the relation

$$B = (1 + \kappa_s) \mu_0 H_s = \text{const} \quad (2)$$

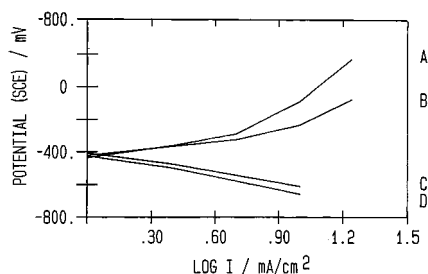


Figure 4. Measured anodic and cathodic polarization curves for two different working electrodes with (B and C) and without (A and D) exposure to a 800 mT magnetic field. The working electrodes were made of iron, the electrolyte was 1 M iron(III) sulfate, and the stirring rate was 120 revolutions/min.

TABLE 6: Effect of a 800 mT Magnetic Field on the Electrode Current through an Iron Electrode Immersed in a Buffered Iron(III) Sulfate Solution (pH = 0.65) at Different Electrode Potentials

electrode potential (SCE) [mV]	current density without B field [mA/cm ²]	current density with B field [mA/cm ²]	difference [mA/cm ²]
-1300	-34.8	-33.7	-1.1
-500	2.9	6.4	3.5
700	9.3	10.6	1.3

we can write

$$W_s = \frac{B^2}{2\mu_0(1 + \kappa_s)} \quad (3)$$

The magnetic driving force applied to the solution can be written as

$$\vec{f}_m = -\nabla W_s = \frac{B^2}{2\mu_0(1 + \kappa_s)^2} \nabla \kappa_s = \frac{B^2 \alpha}{2\mu_0} \nabla C_p \quad (4)$$

where $\alpha = d\kappa_s/dC_p$. This magnetic force must be added to the other forces in the Navier–Stokes equation describing solution flow in the system.

$$\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} = \nu \nabla^2 \vec{v} - \frac{\nabla P}{\rho} + \vec{g} + \frac{\vec{f}_m}{\rho} \quad (5)$$

The equation of continuity can be written in the form

$$(\nabla \cdot \vec{v}) = 0 \quad (6)$$

Equations for ionic transport for i th component of the solution can be written as

$$(\nabla \cdot \vec{j}_i) = 0, \quad i = 1, 2, 3 \quad (7)$$

where the flux density can be represented in general form as the sum of three contributions

$$\vec{j}_i = \vec{j}_{\text{dif}} + \vec{j}_{\text{migr}} + \vec{j}_{\text{conv}} \quad (8)$$

where the subscripts are diffusion, migration, and convection.

Finally, we must add a condition of local electroneutrality in solution:

$$\sum_i z_i C_i = 0 \quad (9)$$

Equations 5–9 give the general formulation of the magnetoconvection effect in electrochemical systems. The main idea

TABLE 7: Changes in the Electrode Potential When Exposed to 300 mT Magnetic Fields with Different Rise Times

dB/dt [mT/s]	change in potential [mV]
20	14
32	14
42	14
300	14

of the theory can be easily formulated as follows. In the presence of a magnetic field in solution, where a gradient of concentration of paramagnetic ions exists as a result of some electrode reaction in which they participate, an additional driving force acting on the solution will arise. This force will cause a redistribution of velocities in the diffusion layer. As a result, an additional convective transport of all the components of solution will be generated. Correspondingly limiting currents of reactions proceeding in electrochemical systems will become a function of applied magnetic field strength or magnetic flux density B .

Experimentally, the system that has been studied in detail is the iron electrode immersed in a solution containing trivalent paramagnetic cations (Fe^{3+}) and bivalent diamagnetic anions (SO_4^{2-}). The dissolution of iron will increase the concentration of the bivalent diamagnetic cations (Fe^{2+}). To simplify, a mathematical model is developed in the case of only bivalent paramagnetic and diamagnetic cations, and diamagnetic anions. This general scheme will be applied below to a case of a corrosion process at an iron electrode in a solution containing paramagnetic cations Co^{2+} and anions SO_4^{2-} . Dissolution of iron will result in an increase of concentration of Fe^{2+} ions in the diffusion layer. We will use for simplicity an assumption that diffusion coefficients of Fe^{2+} , Co^{2+} , and SO_4^{2-} ions are approximately equal to each other, $D_1 = D_2 = D_3 = D$, and will use the Nernst model of a diffusion layer having a thickness L , which will be considered below as a phenomenological parameter. In accordance with the Nernst model, we will assume that in the absence of a magnetic field, the solution in the diffusion layer is immobile. A set of electrodiffusion equations in the diffusion layer for a system under consideration can be represented as follows:

$$2FD \left(\frac{dC_1}{dX} + 2C_1 \frac{F}{RT} \frac{d\varphi}{dX} \right) + 2F\nu_m C_1 = -I_{\text{corr}} \quad (10)$$

$$2FD \left(\frac{dC_2}{dX} + 2C_2 \frac{F}{RT} \frac{d\varphi}{dX} \right) + 2F\nu_m C_2 = -I_{\text{corr}} \quad (11)$$

$$2FD \left(\frac{dC_3}{dX} - 2C_3 \frac{F}{RT} \frac{d\varphi}{dX} \right) + 2F\nu_m C_3 = 0 \quad (12)$$

$$C_1 + C_2 = C_3 \quad (13)$$

Here, I_{corr} is a corrosion current density under the conditions of an open circuit and C_1 , C_2 , and C_3 are concentrations of Fe^{2+} , Co^{2+} , and SO_4^{2-} ions, respectively.

Boundary conditions for eqs 10–13 can be formulated in the form

$$C_1(X=L) = 0; \quad C_2(X=L) = C_3(X=L) = C^0; \quad \varphi(X=L) = 0 \quad (14)$$

Introducing dimensionless variables,

$$c_i = \frac{C_i}{C^0}, \quad x = \frac{X}{L}, \quad c_i = \frac{C_i}{C^0}, \quad \psi = \frac{F\varphi}{RT},$$

$$i_{\text{corr}} = \frac{I_{\text{corr}}L}{FDC^0}, \quad \tilde{v}_m = \frac{v_m L}{D} \quad (15)$$

we can rewrite eqs 10–14 in the form

$$\frac{dc_1}{dx} + 2c_1 \frac{d\psi}{dx} + \tilde{v}_m c_1 = -\frac{i_{\text{corr}}}{2} \quad (16)$$

$$\frac{dc_2}{dx} + 2c_2 \frac{d\psi}{dx} + \tilde{v}_m c_2 = \frac{i_{\text{corr}}}{2} \quad (17)$$

$$\frac{dc_3}{dx} - 2c_3 \frac{d\psi}{dx} + \tilde{v}_m c_3 = 0 \quad (18)$$

$$c_1 + c_2 = c_3 \quad (19)$$

$$c_1(1) = 0, \quad c_2(1) = c_3(1) = 1, \quad \psi(1) = 0 \quad (20)$$

Case of “Weak” Magnetic Fields. We shall analyze the problem below using a perturbation method considering magnetic terms as a small perturbation of zero-order problem corresponding to the absence of magnetic field in the system.

$$c_i = c_i^{(0)} + c_i^{(1)} \quad (21)$$

$$\psi = \psi^{(0)} + \psi^{(1)} \quad (22)$$

$$\tilde{v}_m = \tilde{v}_m^{(1)} \quad (23)$$

In the zero-order approximation, we have

$$\frac{dc_1^{(0)}}{dx} + 2c_1^{(0)} \frac{d\psi^{(0)}}{dx} = -\frac{i_{\text{corr}}}{2} \quad (24)$$

$$\frac{dc_2^{(0)}}{dx} + 2c_2^{(0)} \frac{d\psi^{(0)}}{dx} = \frac{i_{\text{corr}}}{2} \quad (25)$$

$$\frac{dc_3^{(0)}}{dx} - 2c_3^{(0)} \frac{d\psi^{(0)}}{dx} = 0 \quad (26)$$

$$c_1^{(0)} + c_2^{(0)} = c_3^{(0)} \quad (27)$$

We shall use below the method of solution of electrodiffusion equations described in detail elsewhere.^{28,29}

Summing eqs 24–26 and taking into account eqs 27 and 20, we have

$$2\frac{dc_3^{(0)}}{dx} = 0, \quad c_3^{(0)}(x) = 1 \quad (28)$$

From eq 26, it then follows that $d\psi^{(0)}/dx = 0$ and

$$\frac{dc_2^{(0)}}{dx} = \frac{i_{\text{corr}}}{2} \quad (29)$$

$$c_2^{(0)} = \frac{i_{\text{corr}}}{2}(x-1) + 1 \quad (30)$$

The velocity profile in the diffusion layer can be found now from eq 5, taking into account eq 29,

$$v \frac{d^2 \tilde{v}_m}{dx^2} + \frac{B^2 \alpha C^0 L^2 i_{\text{corr}}}{4\mu_0 \rho v D} = 0 \quad (31)$$

Integration of eq 31 with the boundary conditions $\tilde{v}_m(0) = 0$ and $d\tilde{v}_m(1)/dx = 0$ gives

$$\tilde{v}_m(x) = \frac{B^2 \alpha C^0 L^2 i_{\text{corr}}}{4\mu_0 \rho v D} \left(x - \frac{x^2}{2} \right) \quad (32)$$

or

$$\tilde{v}_m(x) = A i_{\text{corr}} \left(x - \frac{x^2}{2} \right); \quad A = \frac{B^2 \alpha C^0 L^2}{4\mu_0 \rho v D} \quad (33)$$

Consider now the first-order approximation for c_i and ψ .

$$\frac{dc_1^{(1)}}{dx} + 2c_1^{(0)} \frac{d\psi^{(1)}}{dx} + \tilde{v}_m c_1^{(0)} = 0 \quad (34)$$

$$\frac{dc_2^{(1)}}{dx} + 2c_2^{(0)} \frac{d\psi^{(1)}}{dx} + \tilde{v}_m c_2^{(0)} = 0 \quad (35)$$

$$\frac{dc_3^{(1)}}{dx} - 2c_3^{(0)} \frac{d\psi^{(1)}}{dx} + \tilde{v}_m c_3^{(0)} = 0 \quad (36)$$

$$c_1^{(1)} + c_2^{(1)} = c_3^{(1)} \quad (37)$$

Summation of eqs 34–36 and taking into account eqs 37 and 28 give

$$\frac{dc_3^{(1)}}{dx} + \tilde{v}_m(x) = 0 \quad (38)$$

Integration of eq 38 with boundary condition $c_3^{(1)}(1) = 0$ results in

$$c_3^{(1)}(x) = A i_{\text{corr}} \left[\left(\frac{x^3}{6} - \frac{x^2}{2} \right) + \frac{1}{3} \right] \quad (39)$$

Expressing $d\psi^{(1)}/dx$ from eq 36, taking into account eq 39, we have $d\psi^{(1)}/dx = 0$. Then from eq 35 follows a differential equation for $c_2^{(1)}(x)$:

$$\frac{dc_2^{(1)}}{dx} + A i_{\text{corr}} \left(x - \frac{x^2}{2} \right) \left[\left(\frac{i_{\text{corr}}}{2} \right) (x-1) + 1 \right] = 0 \quad (40)$$

Integration of eq 40 with the condition $c_2^{(1)}(1) = 0$ gives

$$c_2^{(1)}(x) = A i_{\text{corr}} \left\{ \left[\frac{i_{\text{corr}}(x^4 - 4x^3 + 4x^2)}{16} + \frac{x^3}{6} - \frac{x^2}{2} \right] + \left[\frac{1}{3} - \frac{i_{\text{corr}}}{16} \right] \right\} \quad (41)$$

Taking the condition for the limiting corrosion current $c_2(0) = c_2^{(0)}(0) + c_2^{(1)}(0) = 0$, we obtain the relationship

$$1 - \frac{i_{\text{corr}}^l}{2} + A i_{\text{corr}}^l \left(\frac{1}{3} - \frac{i_{\text{corr}}^l}{16} \right) = 0 \quad (42)$$

From the last relationship, it follows that at small A values

$$i_{\text{corr}}^l \approx 2 + \frac{5}{6}A \quad (43)$$

In dimensional form we finally have

$$i_{\text{corr}}^{\text{l}} = \frac{2FDC^0}{L} + \frac{5FB^2\alpha(C^0)^2L}{24\mu_0\rho\nu} \quad (44)$$

It can be seen from eq 43 that when A increases, $i_{\text{corr}}^{\text{l}}$ increases linearly. According to eq 42, as A increases, i.e., B increases, $i_{\text{corr}}^{\text{l}}$ tends asymptotically to a plateau corresponding to $i_{\text{corr}}^{\text{l}} = 16/3$.

Case of "Strong" Magnetic Fields. Consider now the situation when dimensionless parameter A describing magnetic field effects is large; $A \gg 1$. In this case, as can be seen from eqs 5 and 6, the velocity \tilde{v} will increase from $\tilde{v} = 0$ at $x = 0$ in a narrow layer and stay practically constant and equal to $\tilde{v} = i_{\text{corr}}/2$ in the rest of the Nernst diffusion layer. This distribution of velocity can be found from

$$\frac{1}{A} \frac{d^2\tilde{v}}{dx^2} - \tilde{v} + \frac{i_{\text{corr}}}{2} = 0 \quad (45)$$

and can be represented in the form

$$\tilde{v} = \frac{i_{\text{corr}}}{2}(1 - e^{-x\sqrt{A}}) \quad (46)$$

Thus, inserting eq 46 into eq 17 and taking into account that $d\psi/dx = 0$, we have

$$\frac{dc_2}{dx} + \frac{i_{\text{corr}}}{2}(1 - e^{-x\sqrt{A}})c_2 = \frac{i_{\text{corr}}}{2} \quad (47)$$

Solution of eq 47 satisfying boundary condition $c_2(1) = 1$ can be represented in the form

$$c_2(x) = e^{-(i_{\text{corr}}/2)\int_0^x (1-e^{-x'\sqrt{A}})dx'} \left[\frac{i_{\text{corr}}}{2} \int_1^x e^{(i_{\text{corr}}/2)\int_0^{x'} (1-e^{-x''\sqrt{A}})dx''} \int_0^{x'} e^{(i_{\text{corr}}/2)\int_0^{x''} (1-e^{-x'''\sqrt{A}})dx'''} dx' + e^{(i_{\text{corr}}/2)\int_0^1 (1-e^{-x'\sqrt{A}})dx'} \right] \quad (48)$$

Taking into account eq 48 with $c_2(0) = 0$, we come to the equation for the limiting current

$$\frac{i_{\text{corr}}^{\text{l}}}{2} = \frac{e^{(i_{\text{corr}}/2)\int_0^1 (1-e^{-x'\sqrt{A}})dx'}}{\int_0^1 e^{(i_{\text{corr}}/2)\int_0^{x'} (1-e^{-x''\sqrt{A}})dx''} dx'} \quad (49)$$

Taking into account that $A \gg 1$, one can find the approximate expression for the limiting current

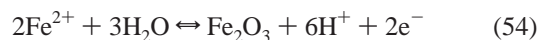
$$i_{\text{corr}}^{\text{l}} \approx 2\sqrt{A} \quad (50)$$

Comparing eqs 43 and 50, we see that the limiting corrosion current linearly increases at small A values and depends as the square root of A at large values, or in other words the magnetoconvective contribution to the limiting current is proportional to B^2 at relatively small B values and at large B values increases linearly with B .

Discussion

In this section, a discussion of the experimental findings and the developed theory is carried out. The experimental results obtained by the open-circuit and potentiostatic/galvanostatic methods are treated separately.

Considering the experiments carried out with 0.1–2.0 M iron(III) chloride solutions where pH values were in the range 1.81–0.33, and 0.5 and 1.0 M iron(III) sulfate solutions where pH values were 0.86 and 0.35, respectively, and according to the Pourbaix diagram (pH/E(SHE) diagram), the following electrode reactions occur:³¹



However, other electrode reactions can occur, but no experiments were carried out under conditions where they occur. Therefore, they are not taken into consideration. Considering the experiments carried out with iron(III) chloride solutions, no chlorine gas evolution takes place.³¹

Considering the experiments carried out with the nickel or cobalt systems at various pH values (Table 2) and according to the Pourbaix diagram (pH/E(SHE) diagram), the main reactions under these conditions are³¹



In addition, possible hydrogen gas evolution, given in eq 53, can occur.

Consider the results obtained by the open-circuit method. Like results obtained from the previous experiments,^{20–22} results from this study show that the effect was only observed in systems consisting of ferromagnetic electrodes immersed in paramagnetic solutions. According to Table 5, the effect was observed in both systems consisting of ferromagnetic electrodes and its paramagnetic metal ion and in systems consisting of ferromagnetic electrodes and other paramagnetic metal ions. In these systems a gradient of concentration of paramagnetic ions near the electrode surface exists because of some electrode reactions in which they participate. However, a gradient of concentration of paramagnetic causes a gradient in the magnetic susceptibility in the solution.

The results given in Table 4 show an increase in the electrode potential for the iron/iron(III) chloride and the iron/iron(III) sulfate systems and a decrease in the potential for both the nickel/nickel chloride and nickel/nickel sulfate systems and the cobalt/cobalt(II) chloride and cobalt/cobalt(II) sulfate systems. To obtain these changes, eqs 51 and 52 are both shifted to the right, while eq 53 is approximately at equilibrium, and eq 54 is shifted to the left; i.e., no precipitation of iron(III) oxide on the electrode surface takes place. Further, eqs 55 and 56 are both shifted to the right, and eq 53 is approximately at equilibrium. Consequently, a transport of the paramagnetic Fe^{3+} , Ni^{2+} , and Co^{2+} ions from the electrode due to the applied magnetic field has to occur. As a secondary effect, there is also a transport of anions to the electrode.

The results given in Figures 1 and 3 show that the magnetic field effect increases with increasing magnetic flux density in a nonlinear relationship. This is in accordance with eqs 33 and 44 and predicts that the limiting current is proportional to B^2 at relatively small B values and tends asymptotically to a plateau at large B values.

The results given in Table 5 show that the magnetic field effect decreases when a diamagnetic solution is added to the paramagnetic solution. The effect decreases with increasing concentration of the diamagnetic electrolyte. As the paramagnetic solution is mixed with a diamagnetic solution, the gradient in magnetic susceptibility at the electrode surface will decrease, and consequently, the magnetic field effect decreases with decreasing magnetic susceptibility of the solution. This is in accordance with eq 44, which predicts that the magnetic field effect is proportional to the gradient in the magnetic susceptibility.

Concerning possible induced transient effects when the magnetic field was turned on and off, the results given in Table 7 show no effect of the rate of change of the magnetic field. Concerning possible induction effects caused by the field emission from the external sources, the experiments were carried out with the iron electrode immersed in distilled water. This is because if the magnetic field effect is due to induced currents in the electrode and the conductors, the effect is expected to be seen. The result, which is given in Table 4, shows no effect of the magnetic field. This indicates that the observed magnetic field effect cannot, apparently, be explained in terms of electromagnetic induction.

Consider the results obtained by the potentiostatic/galvanostatic method. Concerning experiments carried out under the experimental conditions of anodic and cathodic polarizations (pH given in Table 2), reaction 53 is shifted to the left at the counter and working electrodes, respectively, where hydrogen gas evolution and an increase in pH take place. Concerning reactions 51 and 52 occurring at the surface of the working electrode, reaction 51 is shifted to the right and reaction 52 is shifted to the left at anodic polarizations, and vice versa at cathodic polarizations.

In the case of iron(III) chloride solutions, an increase in the chlorine concentration at the working and counter electrodes takes place under anodic and cathodic polarizations, respectively. However, owing to the polarizations studied, no chlorine gas evolution takes place.³¹

In the case of iron(III) sulfate solutions, there will be an increase in the sulfate concentration at the working and counter electrodes under anodic and cathodic polarizations, respectively.

According to the purposed hypothesis, paramagnetic cations (Fe^{3+} , Ni^{2+} , Co^{2+}) are transferred from the ferromagnetic working electrode to the solution when exposed to a static magnetic field. This is assumed to occur both at anodic and cathodic polarizations, as shown in eq 44. Consequently, the applied current between the working and counter electrode tends to decrease at the anodic polarization and increase at the cathodic polarization when exposed to a static magnetic field. To maintain a constant current under galvanostatic conditions, the anodic polarization has to increase and the cathodic polarization has to decrease; i.e., the electrode potential in both cases tends to move in the positive direction. To maintain a constant potential under potentiostatic conditions, the applied anodic electrode current has to increase. This consideration is based on the assumption that the involved salts are easily soluble.

Results given in Figures 2 and 4 show an increase in both the anodic and cathodic polarizations for the iron/iron(III) chloride system and a decrease in the anodic polarization and an increase in the cathodic polarization for the iron/iron(III) sulfate system due to the magnetic field.

The results obtained with the iron/iron(III) chloride system and the cathodic polarization for the iron/iron(III) sulfate system

are in accordance with the abovementioned electrochemical considerations.

Considering the anodic polarization for the iron/iron(III) sulfate system, the concentration of sulfuric anions at the surface of the working electrode will tend to increase with increasing anodic polarization. Also, according to the reduction of ferric ions at the working electrode, there will be an increase in the concentration of ferrous ions. Since the solubility of $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ is slight (0.56 M in cold water),³² it is assumed that there will be an increased precipitation of iron(II) sulfate on the surface of the working electrode with increasing anodic polarization, which inhibits further ferric reduction reaction. Consequently, a decrease in the anodic polarization due to the magnetic field will occur.

Concerning the cathodic polarization for the iron/iron(III) sulfate system, there will be a decrease in the concentration of sulfuric anions at the surface of the working electrode with increasing polarization. Consequently, it is assumed that the concentration of $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ is less than its solubility and no precipitation, and hence no inhibition of the ferric reduction at the electrode surface, takes place.

According to Table 6, the results from experiments with a buffered iron(III) sulfate solution (pH = 0.65) show that the magnetic field effect depends on the electrode potential. The observed effect was greater at -500 mV (SCE) than at 700 mV (SCE) and at -1300 mV (SCE). At low anodic polarizations, the results obtained by the potentiostatic method showed great fluctuations in the electrode current.²² However, the change in the electrode current due to the magnetic field was the same order magnitude as the fluctuations, and consequently, a small detectable effect of the magnetic field will be obtained. At high cathodic polarization, the transport of cations toward the working electrode was predominating relative to the migration of the paramagnetic cations (Fe^{3+}) to the working electrode when exposed to the magnetic field. Consequently, the relative change in the electrode current was small, and the detectable effect of the magnetic field will be expected to be small. At polarization in between, the migration of the paramagnetic cations (Fe^{3+}) toward the working electrode due to the magnetic field is the same order of magnitude as that of the transport of cations toward the counter electrode. Consequently, both eqs 52 and 53 are shifted to the left, the relative change in the electrode current is great, and the magnetic field effect will be detectable.

Concerning the stirring process, the obtained experimental results show a decreased magnetic field effect with increasing stirring rate. As the thickness of the diffusion layer (L) decreases with increasing stirring rate,³⁰ the predicted additional limiting current due to the magnetic field (eq 44) will also tend to decrease. Consequently, the predicted magnetic field effect is in accordance with the obtained experimental results.

Considering the mathematical development, eq 44 describes intensification of the corrosion process in the presence of a magnetic field. It is useful to note several interesting aspects of received expression. The magnetic term in eq 44 is proportional to the square of the solution concentration, while the first term corresponding to limiting current in binary solution in the absence of a magnetic field is linear with C^0 . Thus, with the increase of solution concentration, the relative contribution of magnetic term will increase. The magnetic term in eq 44 is proportional to L . This explains the observed decrease of the magnetic field influence when the solution was stirred, and correspondingly, L decreased. The magnetic term also contains the density of solution and its viscosity, and experimental results prove that these dependencies exist. As seen from eqs 4, 31,

and 32, the velocity of ion transport induced by the magnetic field is directed from the electrode into solution. To complete the mathematical description of the magnetic field effect, the case of "strong" magnetic fields is also taken into consideration. In this case the magnetoconvective contribution to the limiting current is proportional to B^2 at relatively small B values and to B at large B values (eqs 33 and 50).

Conclusion

The effect of static magnetic fields on electrochemical systems was observed only within systems consisting of ferromagnetic electrodes immersed in paramagnetic solutions. In these systems a gradient in the magnetic susceptibility in the solution at the electrode surface exists owing to the gradient of concentration of paramagnetic ions that participate in some electrode reactions.

The experimental results showed that the magnetic field caused an anodic polarization for the ferric/ferrous system and a cathodic polarization for the nickel/nickel-ion and the cobalt/cobalt-ion system. The observed magnetic field effect increased with increasing magnetic flux density and electrolyte concentration and decreased with increasing temperature and stirring rate and when the paramagnetic solutions were mixed with diamagnetic solutions. The results were obtained by the open-circuit potential and the potentiostatic/galvanostatic methods.

The suggested interaction mechanism is magnetoconvection, which predicts that to obtain any magnetic field effect, there has to exist a gradient in the magnetic susceptibility in the solution at the electrode surface through which the magnetic field causes an additional convective transfer of all components of the solution. The magnetic driving force applied to the liquid has the same direction as the gradient of paramagnetic ions. Further, the suggested mechanism predicts that the magnetic field effect increases with increasing magnetic flux density and magnetic susceptibility of the solution and decreases with increasing temperature and stirring rate.

The evidence presented here shows that the proposed hypothesis and the proposed interaction mechanism are verified.

Glossary

B	magnetic flux density (T)
C, C^0	concentration, bulk concentration (mol/m ³)
D	diffusion constant (m ² /s)
F	Faraday constant (C/mol)
\vec{f}	magnetic driving force (N/m ²)
g	acceleration of gravity (m/s ²)
H	magnetic field strength (A/m)
I, \vec{j}	current density (A/m ²)
j	flux density (mol m ⁻² s ⁻¹)
L	thickness of diffusion layer (m)
P	pressure (Pa)
R	universal gas constant (J/K)
t	time (s)
T	temperature (K)
\vec{v}	velocity of the solution (m/s)

W	density of energy of magnetic field (J/m ³)
X	distance from electrode surface (m)
z	number of electrical charges
φ	electrical potential (V)
κ	magnetic volume susceptibility
μ_0	magnetic permeability for vacuum (H/m)
ν	kinematic viscosity (m ² /s)
ρ	density (kg/m ³)

Subscripts

corr	due to corrosion
i	ion of kind i
m	due to magnetic field
p	paramagnetic ion
s	solution

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