

Magnetic Field Effect on Electrode Reactions.

I. Effects on the Open-Circuit Potential of Electrodes in Solutions of Different Magnetic Properties

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Waskaas, M. 1996, Magnetic Field Effect on Electrode Reactions. I. Effects on the Open-Circuit Potential of Electrodes in Solutions of Different Magnetic Properties. – Acta Chem. Scand. 50: 516–520 © Acta Chemica Scandinavica 1996.

Experimental results show that static magnetic fields increase the open-circuit potential of a ferromagnetic iron electrode in a paramagnetic iron(III) chloride solution. The observed effect depends on the magnetic flux density and the electrolyte concentration. However, a saturation phenomenon is observed above 700 mT. The obtained effect of the magnetic field also shows a dynamic behavior with time constants of 13.1 ± 4.3 and 8.1 ± 2.2 s for 1.0 M iron(III) chloride solutions at magnetic flux densities of 400 and 810 mT, respectively. Combinations of other electrode materials (iron, nickel, platinum, zinc and copper) and electrolytes [iron(II) chloride, iron(II) sulfate, iron(II) oxide, iron(III) oxide, nickel(II) chloride, zinc chloride and copper(II) chloride] showed no effect of the magnetic field.

Results from many experimental and theoretical studies show that magnetic fields exert a perceptible influence on the electrode processes in an electrochemical cell. Some of them indicate that a static magnetic field may cause a change in the potential between the two electrodes in an electrochemical cell with flowing electrolyte.^{1–6} Results from other studies indicate that the magnetic field may cause an increased diffusional mass transport at the electrodes.^{6–17} The observed effects have been explained in terms of magnetohydrodynamics.

The purpose of this study is to examine experimentally the possible effects of static magnetic fields on the electrical potential of electrodes in solutions of different magnetic susceptibilities and magnetic permeabilities.

In the case of stirred solutions, there will be a flow of positive and negative ions within the solution. When exposing such a solution to a static magnetic field, there will be an effect of the field upon the flow of ions due to the Lorentz force, and hence, this interaction may cause a possible effect in addition to a possible effect of the static magnetic field due to the magnetic properties of the electrode and the solution.¹⁸ Therefore, to examine a possible effect of the static magnetic field only due to the magnetic properties of the electrode and the electrolyte, unstirred solutions are used.

Experimental

Apparatus. The experimental setup is shown in Fig. 1. An exposure chamber was placed between the poles of

an electromagnet, which produced a static field with magnetic flux densities up to 810 mT. The magnetic poles were circular with a diameter of 10 cm and an area of 78.5 cm^2 . The gap between the poles was 3.0 cm.

The exposure chamber, which consisted of two parts, was made of Teflon plastic and is shown in Fig. 2. The

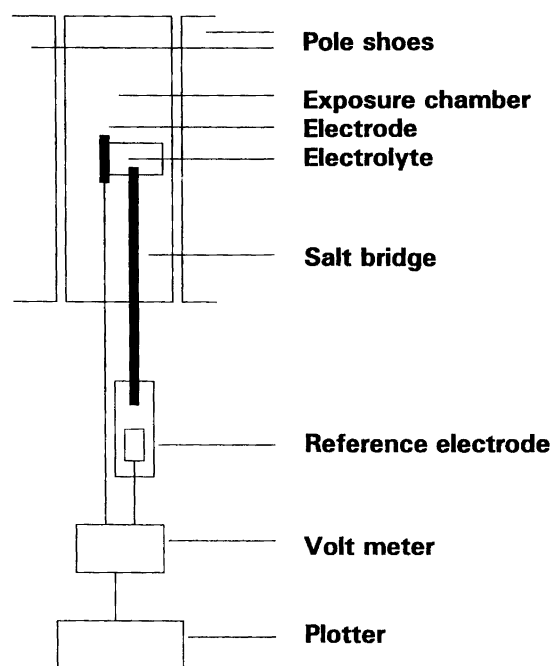


Fig. 1. The experimental setup.

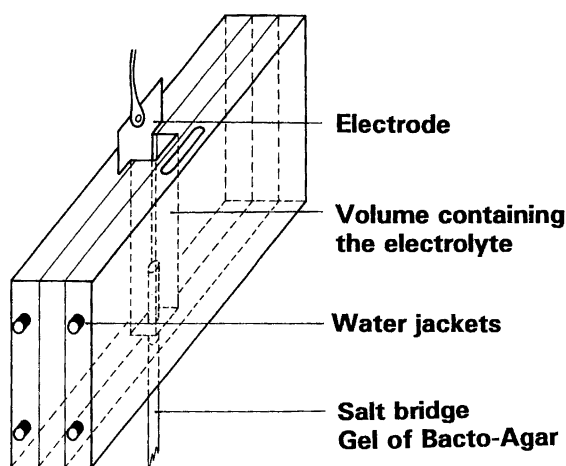


Fig. 2. The exposure chamber.

two parts of the chamber were held together with screws of a non-magnetic material (brass). The dimensions of the exposure volume containing the electrolyte were $1 \times 1 \times 4 \text{ cm}^3$. A plug of rubber with two connection tubes for gas, where the gas passed through in opposite directions, was set on the top of the volume.

All electrodes used in the exposure chamber were rectangular and had an area of $1 \times 4 \text{ cm}^2$ and a thickness of 0.7 mm. They were put vertically in the exposure chamber and placed perpendicular to the field in the middle of the magnetic gap. The magnetic flux density was measured to be homogeneous all over the electrode within an accuracy of 1 mT. To tighten, a gascheck ring of rubber was put around the electrode. The exposure chamber was temperature-controlled by a water jacket through which water circulated to and from an ultrathermostat.

The reference electrode (a standard calomel electrode) was placed into a solution in a chamber outside the magnetic field, as indicated in Fig. 1. The solution was the same and with the same concentration that was used in the exposure chamber. Between the exposure chamber and the reference chamber, there was a salt bridge which consisted of a tube containing a gel of Bacto-Agar. Above the electrolyte in both chambers an atmosphere of argon was used. The distance between the two chambers was 30 cm. The voltage between the electrodes was measured by a voltmeter and printed out by a printer connected to the voltmeter.

The solutions were prepared from the respective crystals with freshly double-distilled water. They were de-aerated with argon, stored under an argon atmosphere and kept under an argon atmosphere during measurements.

The exposing electrodes used were made of the following materials: iron (St 12-03 DIN 1623), nickel, platinum, zinc and copper. The electrolytes used were iron(III) chloride, iron(II) chloride, iron(II) sulfate, iron(II) oxide, iron(III) oxide, nickel(II) chloride, zinc chloride and copper(II) chloride.

The electrodes of iron and nickel have ferromagnetic properties, while platinum has paramagnetic properties. The electrodes of zinc and copper have diamagnetic properties. The electrolytes of iron(III) chloride, iron(II) chloride, iron(II) sulfate, iron(II) oxide, iron(III) oxide, nickel(II) chloride, zinc chloride and copper(II) chloride have all paramagnetic properties, while zinc chloride has diamagnetic properties.¹⁹

Experimental procedure. For each experiment the following preparation procedure was carried out. New electrodes were polished and then washed in a solution of chlorinhydride before using them in the experiments. The exposure chamber was taken apart, the electrode was removed and the chamber was cleaned by distilled water and then dried. A new electrode was put in place, and the exposure chamber was put together. A fresh solution of electrolyte (3 ml) was filled into the exposure chamber, and the rubber plug was put into the top of the volume. A small stream of argon was then fed through the plug. The exposure chamber was then placed in the magnetic gap. The temperature was controlled and held at $25 \pm 0.5^\circ \text{C}$ for both exposed and unexposed solutions. The voltage measurements started at the same time as the exposure chamber was placed in the magnetic gap. After the end of each experiment the whole preparing procedure was done over again.

Four different types of experiments were carried out during this study: (1) voltage measurements as a function of magnetic flux densities, and salt concentration, (2) measurements of possible long-term effects, (3) computations of possible time constants and finally, (4) studies of possible induction effects.

(1) By the voltage measurements as a function of the magnetic flux densities for solutions of iron(III) chloride and iron electrode, the exposure schedule was as follows (all magnetic flux densities are given in mT): 0, 140, 0, 280, 0, 400, 0, 520, 0, 600, 0, 720, 0, 810, 0. The time elapsed at each magnetic flux density was 50 s. This exposure schedule above, was used for the concentrations of iron(III) chloride of 0.001, 0.01, 0.1, 0.4, 1.0, 1.5 and 2.0 M.

By the voltage measurements for the other combinations of electrodes and electrolytes than iron electrode and iron(III) chloride, the exposure schedule was: 0, 600, 0 mT. The exposure time and the rate of change of the magnetic field were the same as mentioned above. The electrode materials and the electrolytes, including their concentrations, are listed in Table 1.

(2) Owing to possible long-term effects for the iron electrode and iron(III) chloride (1.5 M), the exposure schedule was: 0, 660, 0, 760, 0, etc. mT. The time elapsed at each magnetic flux density was 50 s. The rate of change of the magnetic field was the same as mentioned above. This exposure sequence was repeated during a period of 3.5 h.

(3) To examine the possible time constants for the system, the step response of first order was used. A step

Table 1. Measurements of possible change in the potential due to 600 mT magnetic field for different combinations of electrodes and electrolytes.

Electrode	Electrolyte	Conc./M
Iron	Iron(II) chloride	1.0
Iron	Iron(II) sulphate	0.5
Iron	Iron(II) oxide	80 g/l
Iron	Iron(III) oxide	115 g/l
Iron	Nickel(II) chloride	1.0
Iron	Zinc chloride	2.0
Iron	Iron(III) chloride	0.1-2.0
Platinum	Iron(III) chloride	1.0
Nickel	Nickel(II) chloride	1.0
Zinc	Nickel(II) chloride	1.0
Zinc	Zinc chloride	2.0
Zinc	Iron(III) chloride	2.0
Copper	Copper(II) chloride	2.0
Copper	Zinc chloride	2.0
Copper	Iron(III) chloride	2.0

in the magnetic flux density was introduced and the voltage was measured as a function of time. The time constant is defined as the time elapsed from introducing the magnetic field to the time when the voltage is increased to $1-(1/e)$ of maximum change. In these experiments, the iron electrode and iron(III) chloride electrolyte with concentrations 1.0 and 2.0 M were used. The magnetic flux densities were 400 and 810 mT. To compute possible significant levels for differences between the different time constants, Student's T-test was used.

(4) The aim of the induction measurements was to examine if the measured effects of the magnetic field was due to induction currents in the electrode and the conductors when the magnetic fields were turned on and off. In this experiment, the iron electrode and 1 M iron(III) chloride electrolyte were used. The magnetic field was increased from 0 to 300 mT at different rise times, and the maximum change in the voltage was measured.

Results

Owing to the exposure schedule previously described, a typical change in the voltage between the iron electrode and the reference electrode due to a certain step in the magnetic field is shown in Fig. 3. The step in the magnetic field was 600 mT, and the electrolyte concentration was 1.5 M.

The measured change in the voltage between the iron electrode and the reference electrode due to the magnetic field is shown in Fig. 4. The electrolyte concentrations were 0.1, 0.4, 1.0, 1.5 and 2.0 M.

In systems containing 0.01 and 0.001 M solutions, no effect of the magnetic field was observed.

According to Fig. 4, a saturation phenomenon in the change in the voltage due to the magnetic field is observed. This maximum change in the voltage seems to increase with increasing electrolyte concentration. In Fig. 5 the maximum change in the voltage is shown as a

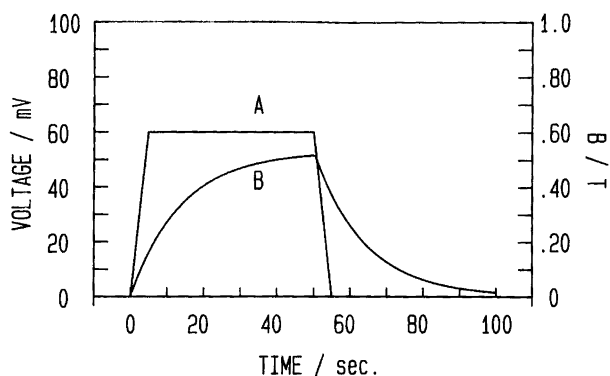


Fig. 3. A typical response of a 600 mT step in the magnetic field (A) on the voltage of the iron electrode relative to the reference electrode (B). The electrolyte concentration of iron(III) chloride was 1.5 M. No stirring.

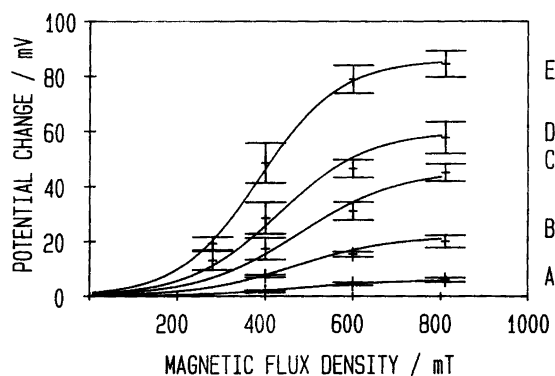


Fig. 4. The measured change in the potential between the iron electrode and the reference electrode as a function of the magnetic flux density. The electrolyte was iron(III) chloride at various concentrations: (A) 0.1, (B) 0.4, (C) 1.0, (D) 1.5 and (E) 2.0 M. No stirring.

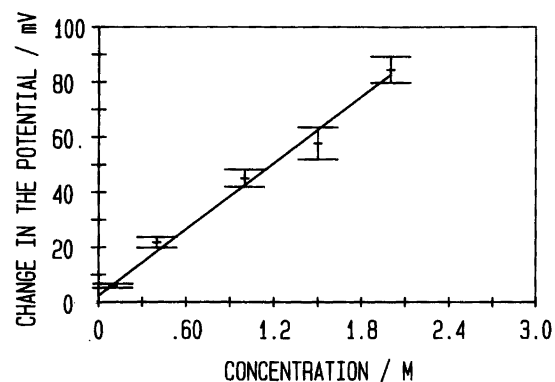


Fig. 5. The maximum change in the potential between the iron electrode and the reference electrode as a function of the concentration of the electrolyte. No stirring.

function of the electrolyte concentration. The iron electrode and iron(III) chloride electrolyte were used.

The initial potential of the iron electrode relative to the standard calomel electrode depends on the electrolyte concentration or activity. These potentials are given in Table 2. In addition, the maximum change of the potential at the different concentrations is given.

Table 2. The initial potential of the iron electrode relative to the standard calomel electrode at different iron(III) chloride concentrations. The maximum changes in the potential and the standard deviation due to the magnetic field are also given.

Conc./ M	No. of experiments	Potential/ mV	Max. change in the potential/mV
0.1	13	-500±8	6.0±1.5
0.4	6	-454±17	21.7±3.8
1.0	14	-421±11	45.1±6.3
1.5	4	-396±11	57.7±11.6
2.0	7	-385±2	84.5±9.5

A long-term effect is shown in Fig. 6. As may be seen, the effect of the magnetic field on the potential of the iron electrode relative to the reference electrode decreases as a function of time.

The calculated time constants for different magnetic fields (400 and 810 mT) and electrolyte concentrations (1.0 and 2.0 M) are given in Table 3. Results from experiments concerning possible induction effects, showed no effects of the rate of change of the magnetic field up to 380 mT s⁻¹.

Using combinations of other electrode materials (iron, nickel, platinum, zinc and copper) and electrolytes [iron(II) chloride, iron(II) sulfate, iron(II) oxide, iron(III) oxide, nickel(II) chloride, zinc chloride and copper(II) chloride], no effect of the magnetic field was observed.

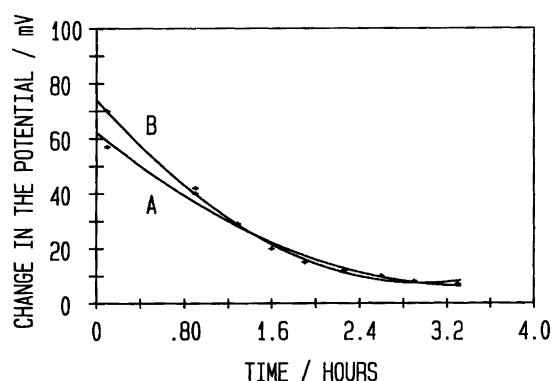


Fig. 6. The measured change in the potential due to the magnetic field as a function of time. Two magnetic flux densities were used: (A) 660 and (B) 760 mT. The electrolyte which was used was 1.5 M iron(III) chloride. No stirring.

Table 3. The measured time constant for 1 and 2 M FeCl₃ electrolyte with magnetic flux density 400 and 810 mT.

Conc./ M	No. of experiments	Flux density/ mT	Mean time constant/s
1.0	12	400	13.1±4.3
1.0	16	810	8.1±2.2
2.0	6	400	8.8±0.9
2.0	8	810	6.6±0.5

Discussion and conclusion

The present experimental results demonstrate that static magnetic fields cause a change in the potential of the ferromagnetic iron electrode in paramagnetic solutions of 0.1 – 2.0 M iron(III) chloride. As shown in Table 2, the iron electrode became more positive when exposed to the magnetic fields.

However, the results indicate that the magnetic field effect occurred within certain limits. In Fig. 4 the changes in the voltage between the iron electrode and the reference electrode versus magnetic flux density are plotted. Below ca. 200 mT, only a small change in the potential was observed. Between 200 mT and ca. 700 mT there was a significant increase in the potential, and above 700 mT a saturation phenomenon was observed. This holds for all the electrolyte concentrations.

The results given in Figs. 4 and 5 show that the effect of the magnetic field increases with increasing electrolyte concentration. From Fig. 5 the maximum effect of the magnetic field seemed to be proportional to the initial concentration of iron(III) chloride.

According to Table 3 the response of the system showed a dynamic behaviour. The response was significantly ($P \leq 0.02$) faster at higher electrolyte concentrations and at higher magnetic flux densities.

According to Fig. 6 the effect of the magnetic field was observed only within the first 2 or 3 h after the start of the experiment. Considering the reaction between the iron electrode and the iron(III) chloride solution within the small exposure chamber, the concentration of ferric ions decreases with time. Therefore, the observed decrease in the magnetic field effect is suggested to be explained in terms of the decrease in the concentration of ferric ions.

Results from studies concerning possible induction effects show no effect of the rate of change of the magnetic field. This indicates that the observed effect of the static magnetic field may not be due to induced currents either in electrodes, electrolyte or connectors when the magnetic field is turned on and off.

Results from experiments with electrodes and electrolytes other than the iron electrode and the iron(III) chloride showed no effects of 600 mT magnetic field.

Acknowledgement. I thank Prof. T Hurlen at the University of Oslo, Norway and Engineer Inger Hedvig Matveyev, Matveyev & Co., Porsgrunn, Norway for helpful discussions and assistance with this manuscript.

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Received September 18, 1995.