

Magnetic field assisted convection in an electrolyte of nonuniform magnetic susceptibility

R. N. O'BRIEN

Chemistry Department, University of Victoria, Victoria, British Columbia, Canada V8W 3P6

K. S. V. SANTHANAM

Chemical Physics Group, Tata Institute of Fundamental Research, Colaba, Bombay, India

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A nonhomogeneous magnetic field is generated electrochemically in an electrodeposition cell which is also an interferometer. Magnetic field strength near 0.5 T produce a detectable by interferometry convective slow rotation in a diamagnetic electrolyte with electroactive (Cu^{2+}) and indifferent (Mn^{2+}) paramagnetic ions present in an otherwise stagnant solution with the cathode over the anode (C/A). Approximate calculation of forces and flows are attempted.

1. Introduction

In an investigation of the effects of magnetic fields on electrochemical transport processes [1–4] and on the deposition of polymer coatings on electrodes [5,6] by laser interferometry it was noticed that there were some anomalous effects [2–4] that were not easily explained. In particular, when the electrode assembly was such as to preclude any natural convection, that is, the cathode was exactly horizontal and directly above and plane parallel to the anode, which is a condition where density layering should result in a stagnant electrolyte, there was clearly some convection. Because of the small size of the cell, a cylinder (38 mm diam. \times 3 mm thick) with 7.5 and 3 mm electrode separations containing about 0.86 and 0.34 mL of electrolyte, electrokinetic effects were considered unlikely. Such effects, to our knowledge, have only been noticed in interferometric studies during electro dialysis (unpublished work in connection with Spiegler *et al.* [7]).

Cupric ion is paramagnetic and this cell with the cathode over the anode (C/A) produces a curve with a slanted S shape of concentration polarization with decreasing concentration on approaching the cathode face and increasing concentration as the anode face is approached. Clearly a nonuniform induced magnetic field will result when the cell is placed in an otherwise uniform horizontal magnetic field since the magnetic susceptibility varies across the electrolyte between the horizontal electrodes. Nonuniform magnetic fields are usually produced by shaped magnet faces and are commonly used in various devices, usually in the gas phase, such as the classic Stern–Gerlach experiment which established the possibility of opposite electron spins but also in the Gouy balance for liquids and solids.

Nonuniform fields have often been produced in electrolyte solutions (usually of small asymmetry)

and unintentionally, and hence not measured or recorded. In the case of vertical electrodes, the effect of strong magnetic fields have received considerable attention [2–6, 8–10]. The Lorentz force driving this enhanced convection has been duly noted [1–6, 8–10], but convection driven solely by a nonuniform magnetic field in a solution of paramagnetic ions has only been postulated [3]. The idea was proposed to explain why no such effect occurred in a solution of a diamagnetic ion (or its effects were too small to be detected) until an indifferent paramagnetic ion was added. If the magnetic field is not too large and the current density is sufficient, and if the electroactive ion is paramagnetic, then a nonuniform induced field which varies with current density should exist in the solution. Thus, at some time during electrolysis, a quasi-equilibrium should result. Such an equilibrium has been observed when migration just balances diffusion [11]. Conversely, if the electroactive ion is diamagnetic and the added indifferent paramagnetic ion is in sufficient quantity, then rotational convection, with top and bottom flow parallel to the electrodes, will occur. This is analogous to that when the electroactive ion is paramagnetic. An apparent natural convection of the usual form should eventually occur as the indifferent ion accumulates in the diffusion layer of the cathode. In the electroactive paramagnetic ion containing solution, the rotation should occur because the anode solution is drawn into the field, or otherwise the effect may be considered as the difference in force required to displace a paramagnetic ion from a less diamagnetic solution to a more diamagnetic one. For the diamagnetic ion-containing solution, the reverse should occur; however, the diamagnetic ions are usually more than 100 times less effective in producing an asymmetric magnetic field.

We believe that these observed results can be developed into a simple and convincing explanation

using accepted magnetic theory together with some approximate calculations made from previously published interferograms of why convection had been observed in a configuration which should give only stagnant solutions.

2. Theory

Recently the convective effects of magnetic fields at vertical electrodes, where natural convection also occurs, have been investigated [1-6, 8-10]. The enhanced convective velocities can be over 100 times the normal convection velocities [2] when conditions are especially favourable and the resulting current densities much larger [2,10]. The results are easily explained in terms of the right-hand rule and the Lorentz force (that is, at the cathode there is an upward stream of ions, powered by density reduction, flowing over the face of the electrode). With a magnetic field at right angles to the flow and in the horizontal plane, a horizontal force is induced also at right angles to the flow and the field. The vector sum is a velocity of greatly increased magnitude across the face of the electrode at some angle to the horizontal, thus reducing the concentration polarization and resulting in a spiral motion within the bulk solution. If there are no paramagnetic ions present, the flow velocities for the same conditions are approximately one-fifth as large. When there is no independent electrolyte flow, such as natural convection, another explanation must be sought. A slow rotation of the electrolyte in an electrolytic cell with initially stagnant electrolyte has been detected interferometrically with two parts of the closed flow pattern parallel to the surface of the two electrodes.

As noted above, nonuniform fields using shaped magnets are well-known. Nonuniform fields in condensed phases are widely treated, including those induced in liquids, but the condition explained here is when a liquid medium with a varying magnetic susceptibility is subjected to a magnetic field which then

gives rise to an induced magnetic field that varies with the magnetic susceptibility. Jafimenko [12] seems to be the only author who includes this possibility in his work and provides the following expression for force

$$F = -\mu_0(\mu - 1)\frac{H^2}{2}A \quad (1)$$

However, what is needed is the induced magnetic field (\mathbf{B}) which is obtained from

$$\mathbf{B} = (1 + 4\pi\mu_0)\mathbf{H} \quad (2)$$

where \mathbf{H} is the magnetic field (in A m^{-1}) and μ_0 is the magnetic susceptibility *in vacuo* in SI units.

Several texts, for example [18], give the magnetic susceptibilities of cupric sulfate, zinc sulfate, and water in the c.g.s. system per mole which in SI units are 1.67×10^{-2} , -5.6×10^{-4} and -1.65×10^{-4} , respectively, where the negative sign indicates a diamagnetic value. Susceptibilities from most sources vary, usually because of the variation in whether the diamagnetic effect of all paired electrons has been considered especially in the paramagnetic ions, but are generally within a few per cent of those here quoted. In the solutions used (0.1 M cupric and zinc sulfate at natural pH), using these data together with Weidemann's additivity law [14] and Selwood's illustrations [15], both solutions should be diamagnetic as charged to the cell. An approximate calculation shows that cupric sulfate will remain diamagnetic until the solution concentration is above 0.5 M.

In Fig. 1, at the solid copper anode, cupric ions are added to the solution so the magnetic susceptibility should increase ($\mu + \Delta\mu$), otherwise the overall diamagnetic effect should be decreased from the bulk. At the cathode, paramagnetic cupric ions are being plated out and the diamagnetic character of the cathode diffusion layer is increasing ($\mu - \Delta\mu$). It is then possible to say that the anode diffusion layer is less repelled by the magnetic field than that associated with the cathode. The anode diffusion layer (but not the bulk electrolyte solution) will be attracted into the

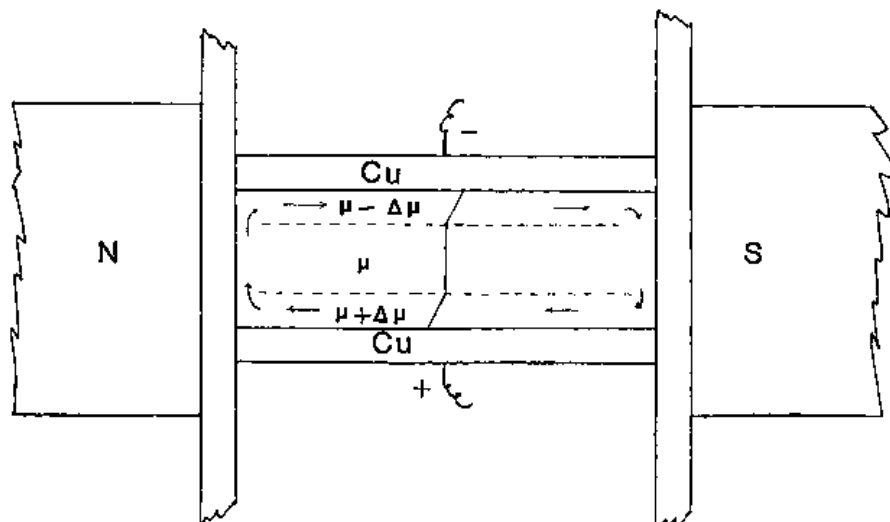


Fig. 1. Schematic representation of the effect of a nonhomogeneous field on a horizontal (C/A) electrodeposition cell.

field differentially to the cathode diffusion layer. From this disparity of repulsions, which has resulted in an apparent attraction of the anode diffusion layer into the field, the rotational motion shown by the arrows in Fig. 1 should occur and as long as an electrolytic current is flowing in the indicated direction an asymmetric induced magnetic field should exist. In the case of a diamagnetic electroactive ion, such as in a zinc sulfate solution, if an indifferent paramagnetic ion is added in enough strength, the rotation described should begin and persist with the indifferent paramagnetic ion tending to accumulate in the diffusion layer of the cathode. However, since a diamagnetic ion is now produced (Zn^{2+}) at the anode and SO_4^{2-} ions are attracted to provide electrical neutrality outside of the electrical double layer, the anode layer should be repelled more by the field than the cathode layer. This effect is also augmented by the migration of Mn^{2+} ions into the cathode region. Hence, the result should be rotation in the opposite direction (counter-clockwise) to that found in 0.1 M CuSO_4 electrolyte (Fig 1). This effect should be detectable in interferograms. Eventually, the rotation should slow down because little difference in magnetic susceptibility will remain between the anode and cathode diffusion layers as the indifferent ion is fed back into the anode layer by a convective flow compensating for its attraction to the cathode by the electric field.

3. Experimental details

The apparatus and procedures have been previously described [1]. Briefly, the electrolytes were natural pH cupric and zinc sulfate with manganous chloride added to the zinc sulfate in some cases. The electrolytes and the plane parallel electrodes were placed in a short cylinder of 38 mm internal diameter. The electrodes were a 3 mm cut from a 38 mm cylinder of the pure metals, which then had varying widths of slices (from 1.1 to 7.5 mm) cut out of the diameter to give two nearly complete semicircles, which were held apart by spacers leaving an active electrode area of 100 mm², allowing for the occlusion of surface by the spacers. The whole electrochemical cell was bounded by reflecting dichroic glass flats such that the cell was also an interferometer. He-Ne laser light was arranged to pass through the cell at a grazing angle to the two electrodes to give transmission interference fringes. A three-pin clamp prevented leaking of the electrolyte and also produced a wedge angle convenient for production of easily video-recorded interference fringes.

4. Results and discussion

In Fig. 1, the interference fringes indicating the concentration of electrolyte between the two electrodes was stylized as three straight lines. Figure 2 is a tracing of interference fringes from data already published [2]. The interferograms were taken after 10, 20,

30, 60, 180 and 300 s of electrolysis at 7.9 mA cm^{-2} . A pair of fringes were traced at each side of the six individual panels taken from video frames to show the variation across a panel. The panels show about one-quarter of the cell width (i.e., about 8.5 mm). The electrolyte was 0.1 M cupric sulfate at 22 °C, and the applied field strength was 0.512 A m^{-1} . Even as early as 10 s there is a difference across the panel, that is, the anode diffusion layer on the left is larger; this grows with time and the increased concentration polarization migrates from side to side. Panel 2 still shows a more extensive anode diffusion layer on the left and the cathode layer is similarly biased. In panel 3 the layers are similar in extent. In panel 4 the cathode layer is still larger on the left but the anode layer is more extensive on the right. In panel 5 the right side shows the greatest extent for both layers and in panel 6 the effect is reversed.

Figure 3 is a tracing of fringes from a previously published [3] interferogram taken at 240 s during electrolysis at 0.59 mA cm^{-2} , 0.435 T with a field of 0.1 M zinc sulfate with 0.1 M manganous chloride added. This shows the beginning of convection. A similar behaviour was observed and recorded when Cr(III) was the added indifferent paramagnetic ion. No detectable rotation or convective effects were present when there were no paramagnetic ions present, that is, when zinc sulfate only was the electrolyte. The first pair of sketched fringes are at the extreme left hand side of the panel. The second pair of sketched fringes occurred at the middle (about 13 mm from the left side of the cell) of the panel. The slight reverse bend just below the cathode diffusion layer is considered to be the result of mild convection, that is, the slow fall of a more concentrated (more dense) parcel of electrolyte. At longer periods of electrolysis (also published as panel (f) in Fig. 9 of [3]) the reverse bends are more pronounced and cover about three-quarters rather than about one-half of the panel. The diffusion layer fringe bends (concentration change) remain closely similar at 2.5 fringe shifts at the cathode and 3.2 at the anode which is opposite to that expected, that is the anode usually has a slightly smaller fringe shift [16]. The general slope of the centre section, originally vertical, increases with time. The 240 s slope is approximately 15° from the vertical and at 600 s, 30°.

The simplest interpretation of the behaviour of the fringes is that the manganous ion is attracted into the cathode diffusion layer (and repelled from the anode diffusion layer) by migration forces reducing the cathode diffusion layer concentration relative to the anode layer. At some time enough of the indifferent cation ion has collected near the cathode to cause that parcel of electrolyte to be more dense than the surrounding electrolyte. In other words, the slow rotation caused by the presence of the paramagnetic manganous ion has caused the manganous ion to be moved to the left until in that area convection begins, which then spreads to the rest of the cathode layer. The convective feeding of manganous ion back to the

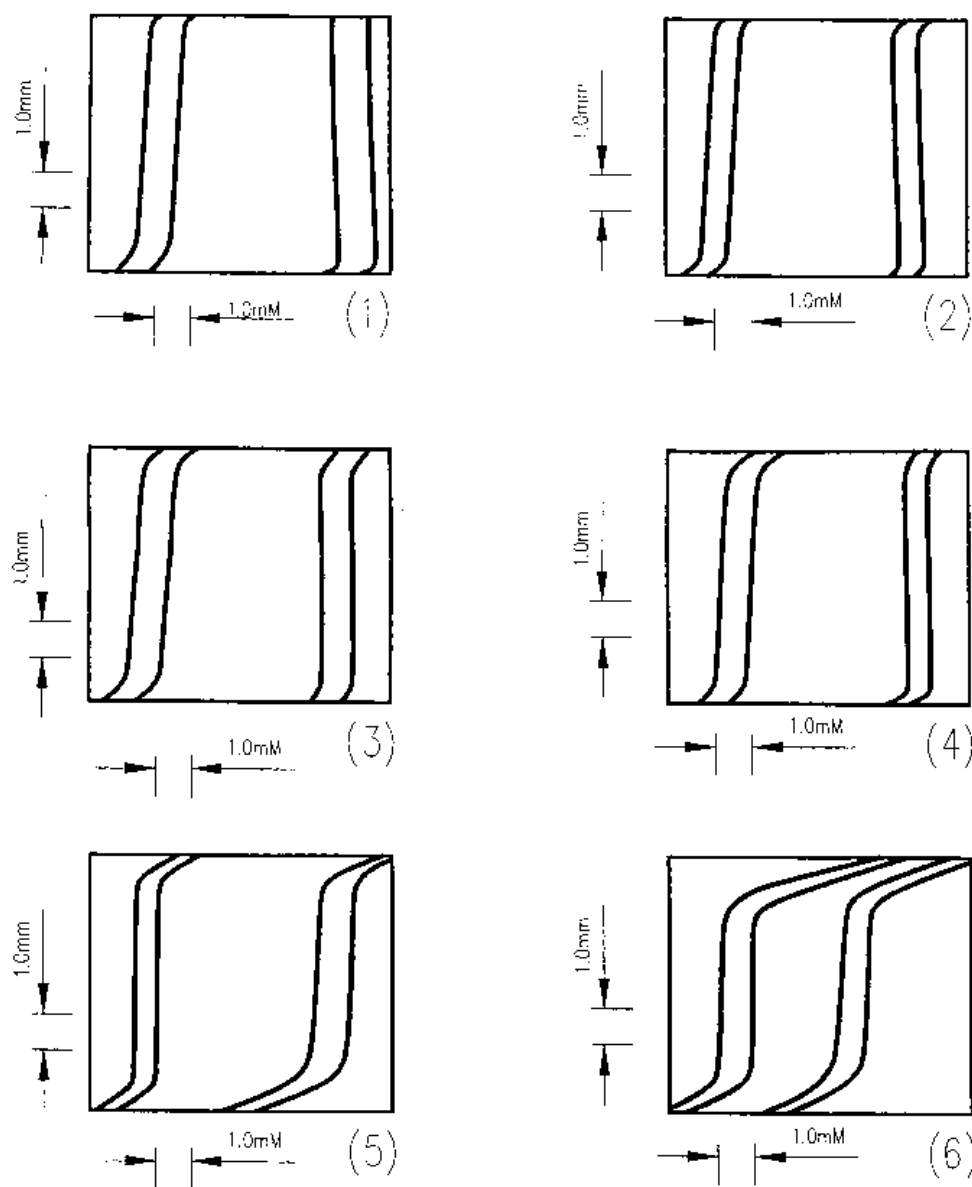


Fig. 2. Pairs of interference fringes (taken from Fig. 9 of [2]) showing abrupt changes in fringe bends (sudden concentration changes) during 300 s of electrolysis at 7.9 mA cm^{-2} in 0.1 M CuSO_4 solution with an imposed magnetic field strength of 0.512 T . Electrolysis times were panels: 1, 10 s; 2, 20 s; 3, 30 s; 4, 60 s; 5, 180 s; 6, 300 s. Electrodes were at the end of the fringes, the vertical marker represents 1 mm , the horizontal 0.001 M CuSO_4 change in concentration at 22°C in a cell 3 mm thick.

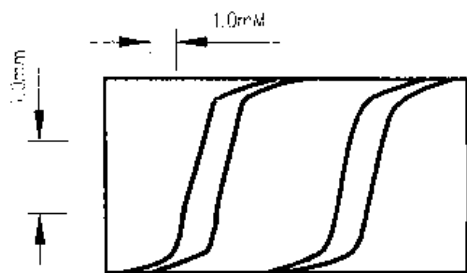


Fig. 3. Two pairs of interference fringes (sketched from panel (e) of Fig. 9 [2]) showing the onset of natural convection in the left hand pair. The indication of convection is the slight reverse bend after 240 s of electrolysis of 0.59 mA cm^{-2} in a solution of 0.1 M ZnSO_4 , 0.1 M MnCl_2 with an applied magnetic field of 0.435 T at an electrode separation of 2.5 mm in a cell 3 mm thick at 22°C . The vertical marker represents 1.0 mm and the horizontal marker 0.001 M ZnSO_4 .

anode area, which must be many times faster than migration to the cathode area (even assisted by the slow rotation) causes the originally vertical centre portion of the fringes to slant to the right increasingly with time until a quasi-equilibrium in Mn^{2+} ions is set up. This would account for the slightly larger fringe shift at the anode.

The evidence for a counter-clockwise rotation for the $\text{Zn}/0.1 \text{ M ZnSO}_4/0.1 \text{ M MnCl}_2/\text{Zn}$ cell rather than clockwise for the $\text{Cu}/0.1 \text{ M CuSO}_4/\text{Cu}$ cell is less dramatic and requires further discussion. As mentioned earlier, at the beginning of electrolysis the anode produces diamagnetic Zn^{2+} , or becomes more diamagnetic and, hence, is more repelled in the field. At the cathode the reduction in concentration of diamagnetic ions, plus the migration into the diffusion layer of paramagnetic Mn^{2+} decreases the diamagnetism of the cathode layer and decreases the

force of repulsion from the magnetic field. Therefore, the forces acting are in the opposite direction to the copper electrodeposition cell. These forces produce a differential repulsion giving an apparent attraction of the cathode layer into the field which should result in a small but finite force for counter-clockwise rotation.

In the case of vertical electrodes for this electrolyte ($\text{ZnSO}_4 + \text{MnCl}_2$) the decrease in required impressed voltage to produce a given density in an applied magnetic field of 0.436 T was 27.2%. This corresponds well with the 40% reduction expected in copper electrodeposition at 0.612 T. This result also follows the observed direct dependence of this variable at vertical electrodes on the product of the field strength and the current density [2]. In the C/A position there is also always a small (max. 25%, min. 2%) but measurable decrease in impressed voltage. Another supporting observation is that with paramagnetic ions present the relaxation time is longer while still in a magnetic field. Our interpretation is that after electrolysis has caused a convective rotation the field continues to produce rotation because of the slowly relaxing diffusion layers containing the indifferent paramagnetic ion and the extended difference (slope of the bulk fringes) in susceptibility to extend the time of concentration polarization relaxation.

Assuming there is merit in these arguments the onset of convection near the centre of the panel after 240 s of electrolysis is consistent with a flow into the field of the diffusion layer impacting on a general migration of Mn^{2+} to the cathode region as observed.

To be certain that the approximate calculation of the degree of diamagnetism of the solutions even with 0.1 M paramagnetic ions present a 0.5 M cupric sulfate solution and several dilutions from it were first run on an AMX 360 nuclear magnetic resonance spectrometer, then in a Gouy magnetic balance. The results are shown in Table 1.

In NMR the recorded frequency shift (Δf) in the solution compared to pure water gives an increasing frequency shift and a reduced peak height and an increased width. At 0.5 M the peak was very broad and of very low amplitude signalling the approach to neutral magnetism (i.e., neither diamagnetic nor

paramagnetic behaviour of the solution). Specifically, as the concentration of the cupric ion in the inner sample (which was surrounded by an annulus of pure water) increases the absorbed energy is decreased, that is, the apparent effective frequency shift of the proton resonance decreases. In the Gouy balance the change in weight or the force on the vial of solution can be converted to the conventional frequency shift value used in NMR by use of the gyromagnetic constant of the proton after the magnetic susceptibility has been calculated for the various concentrations. Table 1 shows some scatter in each type of measurement but good agreement between the two types of measurement and reasonable agreement with calculations from published susceptibility values. A manual plot and slope calculation gave nearly identical values. The solutions used were, then, diamagnetic, but at the anode less diamagnetic than at the cathode for the cupric sulfate experiments.

Crude calculations in an appendix to [2] gave reasonable agreement with the observed rate of flow in the slow rotation. This rate can be approximated by measuring the time (Fig. 2) taken for a given concentration change at the anode to move across half of the panel from panel 4 to panel 5 which was approximately 4.2 mm in 120 s or 0.035 mm s^{-1} . It is clear from the following panels that the system is not at equilibrium, in fact at 7.9 mA cm^{-2} in this small cell it never did achieve an equilibrium. The calculated velocity is therefore an approximate average over the 120 s.

Using Fig. 2 (derived from Fig. 9 of [2]), the fringe shift at the cathode averages 2.1 at 300 s. Using the appropriately modified Bragg equation,

$$N\lambda = 2nt \quad (3)$$

where N is the order of interference, λ is the wavelength of He-Ne laser light and t is the thickness of the cell, all in compatible units, the concentration per fringe shift can be calculated using the data from [17] for the refractive indices for pure water and 0.1 M cupric sulfate at 22.5°C , 1.33341 and 1.33449, respectively, which gives 0.00093 M per fringe shift. A fringe shift has occurred when the end of one fringe has bent to be opposite the centre of the adjacent fringe's straight centre section.

Using Equation 2, and making some reasonable assumptions, a differential susceptibility can be calculated from panel 5 (180 s of electrolysis at a current density of 7.9 mA cm^{-2} with an electrode separation of 7.5 mm) of $4.762 \times 10^{-4} \text{ T}$. This very small field can be transformed into a pressure using

$$P = B^2/2\mu \quad (4)$$

to give the differential force on the cathode and anode diffusion layers [19] a value of $1.219 \times 10^{-3} \text{ N m}^{-2}$. From the interferograms, the combined area of the two diffusion layers was found to be $1.667 \times 10^{-3} \text{ cm}^2$. The mass of the two diffusion layers at 180 s was found to be 0.0042 g. The force of the differential pressure on this mass of solution would produce an

Table 1. Diamagnetic measurements

Experiment	Concentration /M	Δf , NMR / $\text{H}_3\Delta$	Δf , Gouy / $\text{H}_3\Delta$
1	0.5	1194.9	1129
2	0.25	598.4	—
3	0.1	231.5	259
4	0.05	114.5	127
5	0.04	91.7	79
6	0.03	68.0	67
7	0.025	57.5	60
8	0.02	46.7	33
9	0.01	18.6	22

acceleration of $3.65 \times 10^{-3} \text{ cm s}^{-2}$. A plot of the product of the concentration and diffusion layer thickness against time of acceleration was graphically integrated and an effective average time of acceleration for 19 s was found and, hence, an imparted velocity calculated. The result was 0.0695 cm s^{-1} . Compared to the measured velocity, 0.035 cm s^{-1} , the result is about double in value. Considering the approximations that had to be made, and that viscous drag in the small ($3 \text{ mm} \times 7.5 \text{ mm} \times 20 \text{ mm}$) volume of electrolyte was neglected, this can be considered reasonably good agreement.

5. Conclusions

There is good evidence that a continuing but possibly unstable nonuniform magnetic field can be obtained in an electrochemical cell. The conditions required are that the electrodes should preferably be horizontal and plane parallel. Likewise, the applied magnetic field should also be horizontal. Now, when an electrolytic current, and of course a small electrical field, is applied between the two electrodes perpendicular to the magnetic field, the susceptibilities of the diffusion layers at the two electrodes are different, giving rise to a nonuniform induced magnetic field. The onset of a slow rotation of the electrolyte can be detected interferometrically, if the susceptibilities are sufficiently different, the rotation is powered by this unbalanced induced magnetic field. Solutions of diamagnetic ions do not result in detectable effects at concentrations of the order of 0.1 M and an applied field of about 0.5 A m^{-1} . When paramagnetic ions are present in this concentration a movement of electrolyte in a predictable direction is possible. Calculation of forces and flows are approximate but calculated flows correspond well with those observed.

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