Effect of High Magnetic Field on the Silver Deposition from Its Aqueous Solution

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The effects of a high *gradient* magnetic field on the Ag^+/Cu liquid−solid redox reaction were studied. A copper wire was placed on a sheet of chromatography paper wet with silver nitrate aqueous solution. At zero field silver dendrites grew uniformly around the wire. In the presence of a gradient magnetic field (ca. 380 T^2m^{-1}), the dendritic pattern changed drastically. The yield of silver metal increased by about 45%. These results are attributable to the convection of aqueous solution on the surface of the paper which is induced by the magnetic force on the paramagnetic copper ions generated in the reaction.

1. Introduction

The effect of high magnetic field (>2 T) on chemical reactions is one of the current topics in basic and applied chemistry. This is partly because superconducting magnets are becoming popular today and partly because unexpected magnetic phenomena which cannot be observed in a low magnetic field have been discovered in a high magnetic field and these new phenomena have potential for industrial application.

The effects of high magnetic field (<14 T) on photochemical reactions of organic compounds have been investigated very extensively in the last five years.[1] The reversal of the magnetic field effects (MFEs) on the lifetime of short-lived intermediates has been observed under high magnetic field (>2 T). The effects of high magnetic field on chemical equilibrium of hydrogen−ferromagnetic compounds have been reported by Yamaguchi and his collaborators.[2] The Gibbs free energy change which is induced by a magnetic field results in a change in the equilibrium constant. The magnetic orientation of fibrin fiber,[3,4] polymers,[5] and organic crystals[6,7] has been also reported.

Recently, Mogi et al. have reported that the deposition pattern of silver metal from Ag^+/Cu redox reaction is affected by a high homogeneous magnetic field (8 T).[8] This is interpreted in terms of a magnetohydrodynamics mechanism in which diffusion of ions is affected by a Lorentz force. The electrodeposition pattern of silver is also affected by a high magnetic field.[9]

In this paper, we report the effects of a high gradient magnetic field on the Ag^+/Cu liquid−solid redox reaction.[10] The dendritic pattern and yield of silver metal deposited by the reaction are affected significantly by the high gradient field. The results are explained in terms of *magnetophoresis*: A high gradient magnetic field induces convection in the thin layer of solution by attracting paramagnetic copper ions generated by the reaction.

2. Experimental Section

The magnetic fields were applied using a superconducting magnet (Oxford Instrument, Spectromag-1000) whose bore tube (50 $\phi \times$ 370 mm) was installed horizontally. Distribution of the magnetic field $B(z)$ was approximated with a Gaussian distribution (Figure 1), the direction (z-axis) of the magnetic field being taken to be along the bore tube. The maximum strength of the magnetic field (B_{max}) is 8 T at z = 0 mm and that of the gradient magnetic field, $B(z)\ dB(z)/dz$, is ca. 380 T^2 m^{-1} at z = 50 mm. In the following, for simplicity, B_{max} is used as the representative of the magnetic field strength.

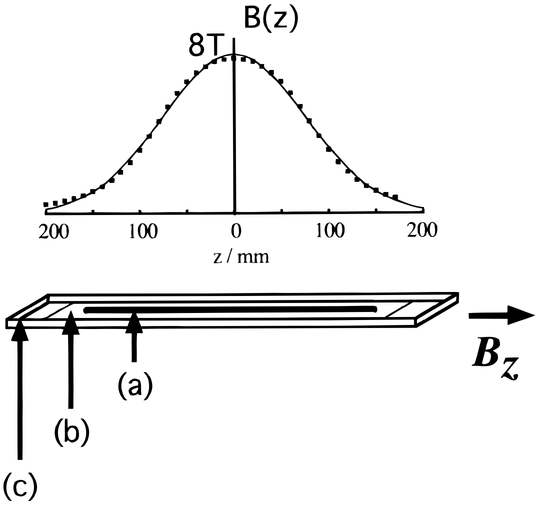

Figure 1. Top: The distribution of the magnetic field $B(z)$. The squares are the observed values, and the solid line is a Gaussian distribution obtained using a least-squares method, respectively. "z" is the distance along the magnetic axis from the center of the magnetic field. The maximum intensity B_{max} is 8 T at z = 0 mm in our experiment. Bottom: The outline of experimental handling: (a) a copper wire (6 $\phi \times$ 250 mm), (b) a piece (37 mm × 300 mm) of chromatography paper soaked with silver nitrate solution (0.5 mol dm^{-3}), and (c) a plastic vessel (40 mm × 380 mm × 10 mm).

Silver nitrate (Nacalai, GR grade) and chromatography paper (Whatman, 1Chr) were used as supplied. Deionized water was used. Copper wire (99.9%, 6 ϕ) and zinc wire (99.99%, 6 ϕ) were polished mechanically and chemically before use.

Liquid−solid redox reaction was carried out in a plastic vessel (37 mm × 380 mm × 10 mm) at room temperature (Figure 1). A copper wire (6 $\phi \times$ 250 mm) was placed on a piece of chromatography paper (40 mm × 300 mm) which was wet with a silver nitrate solution (0.5 mol dm^{-3}, 0.4 mL), as depicted in Figure 1. The vessel was then placed in a bore tube of the magnet so that the center of the vessel coincided with that of the magnetic field. A silver nitrate solution was soaked into a piece of chromatography paper, since a fluid solution is attracted to or repelled from a high gradient magnetic field due to its magnetic susceptibility.[11]

The dendrite of silver metal deposited on the paper was washed twice with dilute hydrochloric acid, 0.1 mol dm^{-3} sodium thiosulfate solution, and water and was dried.

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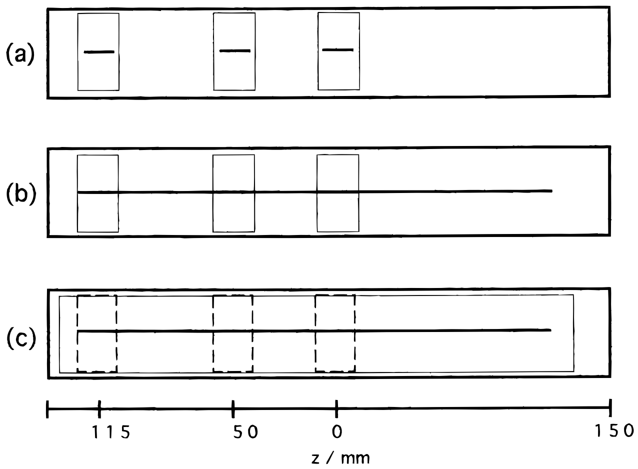

Figure 2. Experimental setup for size effects of chromatography paper and copper wire on the yield of copper ions. (a) Small pieces of copper wire (6 $\phi \times 15$ mm) were placed on small pieces of the paper (37 mm × 20 mm) at $z = 0$, 50, and 115 mm. (b) A copper wire (6 $\phi \times 250$ mm) was placed on pieces of the paper (37 mm × 20 mm) at the same positions. (c) A copper wire (6 $\phi \times 250$ mm) was placed on a long piece of the paper (37 mm × 300 mm). In cases a and b the relative concentration of copper ions was determined at each piece of paper in the absence and presence of a magnetic field ($B_{\max} = 8$ T). In the case of c, after the reaction the paper was cut as indicated by broken lines in the figure, and then the copper concentrations were determined analogously.

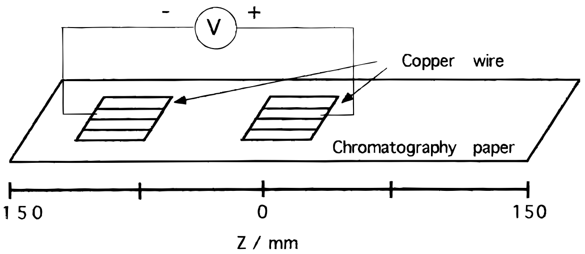

Figure 3. Experimental setup for the electromotive force. Two sets of copper wire (6 $\phi \times 50$ mm × 4) were placed on a piece of chromatography paper at $z = 0$ and $z = 125$ mm.

The distribution of the copper ion generated was detected using the following reaction,

$$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} \qquad (1)$$

Since the tetraammine copper complex ($[Cu(NH_3)_4]^{2+}$) had an absorption band at ca. 630 nm, the area of the paper where Cu^{2+} ion existed became bright blue. Actually, after the redox reaction, the chromatography paper was brought into contact with another chromatography paper wet with aqueous ammonia so that the copper ion on the paper reacted with ammonia before diffusion.

The yield of silver metal was determined by gravimetry. The relative yield of Cu^{2+} was determined using reaction 1. After the redox reaction, the solution adsorbed by the chromatography paper was extracted with water. Ammonia water was added to the extract, and the relative yield of copper ion was calculated from the absorbance of the copper−ammine complex at 630 nm.

Size effects of the chromatography paper and copper wire were examined under the experimental condition schematically shown in Figure 2.

The electromotive force was measured using a high-impedance electric recorder. As shown in Figure 3, the two pieces of copper wire (6 $\phi \times 50$ mm × 4) were placed on a piece of chromatography paper at $z = 0$ and $z = 125$ mm. Magnetic field strengths were 8 ($z = 0$ mm) and 2 T ($z = 125$ mm).

For the purpose of comparison, the effects of the high gradient magnetic field on the Ag^+/Zn redox reaction were examined analogously.

3. Results

3.1. MFE on the Deposition Pattern of Silver Metal and Copper Ion. The liquid−solid redox reaction studied here is given by the following equation:

$$2Ag^+ + Cu \rightarrow 2Ag\downarrow + Cu^{2+} \qquad (2)$$

Because of the order of ionization tendency, the dendrite of silver metal deposits from a silver nitrate solution when a copper wire is placed on the paper. Figure 4 shows the effects of a magnetic field ($B_{\max} = 8$ T) on the deposition pattern of silver metal as a function of time. At zero field, silver metal deposits uniformly around the copper wire with time. When the reaction is carried out in the magnetic field, the dendritic pattern of silver metal is affected drastically: The silver metal does not deposit in the neighborhood of the center of the wire after the 1 h reaction. The dendritic pattern of the metal at $z =$ ca. 75 mm changes remarkably, as shown in Figure 4, although, in the absence of the magnetic field, the dendrite grows almost perpendicular to the long axis (z-axis) of the wire. In the presence of the magnetic field the dendrite tilts to the high magnetic field. The MFE was observed only in the high magnetic field ($B_{\max} \geq$ ca. 5 T).

Figure 5 shows the effect of the magnetic field ($B_{\max} = 8$ T) on the Cu^{2+} ion distribution pattern as a function of time. At zero field the Cu^{2+} ions distribute uniformly around the copper wire. When the magnetic field is applied, the distribution pattern of Cu^{2+} changes. Even after 10 min of reaction, the Cu^{2+} ions shift to the neighborhood of the center part of the paper, which coincides with the center of the magnetic field.

For the purpose of comparison, similar solid−liquid redox reactions shown below were examined:

$$Cu^{2+} + Zn \rightarrow Cu\downarrow + Zn^{2+} \qquad (3)$$

$$2Ag^+ + Zn \rightarrow 2Ag\downarrow + Zn^{2+} \qquad (4)$$

In the case of reaction 3, the deposition of copper metal shifts significantly to the neighborhood of the center of the paper.[12] Figure 6 shows the MFE on the deposition pattern of silver metal generated from reaction 4. In marked contrast to the results of reactions 2 and 3, a high magnetic field ($B_{\max} = 8$ T) does not affect reaction 4.

3.2. MFE on the Yields of Silver Metal and Copper Ion. The MFE on the yield of silver metal was determined by gravimetry. The yield after the 1 h reaction is 53 ± 7 mg at zero field, whereas it is 77 ± 10 mg in the presence of a magnetic field ($B_{\max} = 8$ T). The yield increases by ca. 45%. Figure 7 shows the effect of the magnetic field ($B_{\max} = 8$ T) on the yield of the copper ion. In accordance with the change in the silver metal yield, the yield of the copper ion after the 1 h reaction increases by about 36% in the magnetic field. The Ag^+/Cu redox reaction is enhanced by application of the magnetic field. It is interesting to note that, by application of the magnetic field, the net yields of both silver metal and copper ion increase, even though the deposition of silver is localized at the two ends of the wire.

For the purpose of comparison, the yield of silver metal deposited from the Ag^+/Zn redox reaction (eq 4) was also examined. Since the dendrite deposited from this reaction sticks to both the zinc wire and chromatography paper, the yields could not be determined accurately. The yields were obtained to be 64 ± 12 mg at zero field and 74 ± 21 mg at 8 T after 1 h of reaction. Taking these large standard deviations into account,

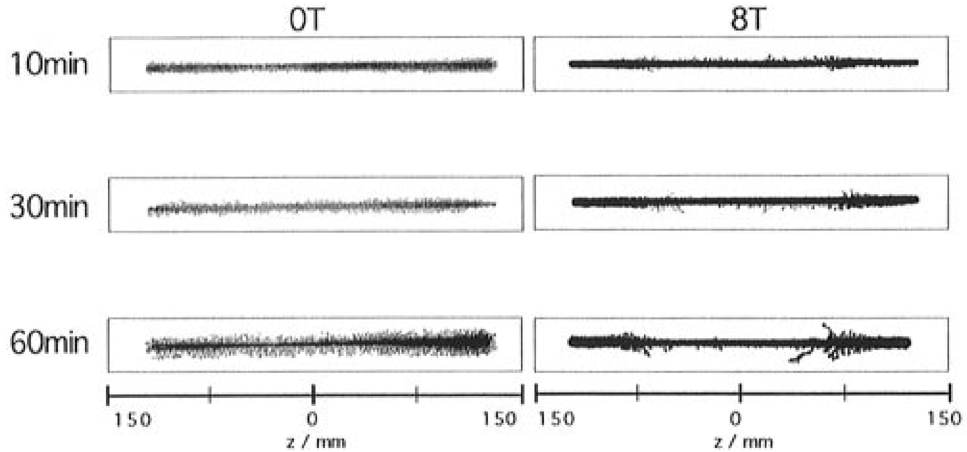

Figure 4. Deposition of silver metal from the Ag^+/Cu reaction in the absence (left) and presence (right) of a magnetic field ($B_{max} = 8$ T). Reaction time is indicated on the left side.

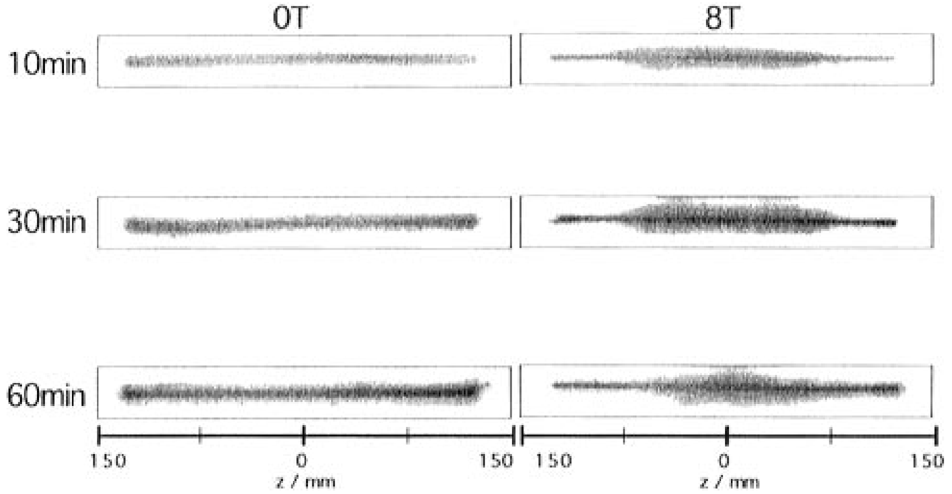

Figure 5. Distribution of copper ions for the Ag^+/Cu reaction in the absence (left) and presence (right) of a magnetic field ($B_{max} = 8$ T). Reaction time is indicated on the left side.

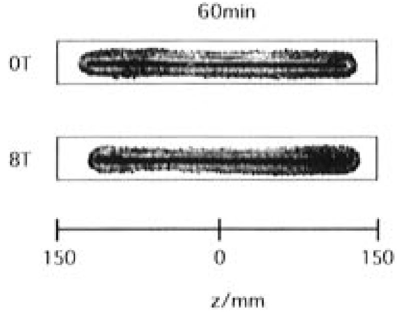

Figure 6. Deposition of silver metal from the Ag^+/Zn reaction in the absence (top) and presence (bottom) of a magnetic field ($B_{max} = 8$ T). Reaction time is 1 h.

the MFE on the deposition yield of silver metal for the Ag^+/Zn redox reaction seems insignificant, if any.

3.3. Influence of the Sizes of Chromatography Paper and Copper Wire on the Yield of Copper Ion. To examine the influence of the sizes of the paper and the wire, the yield of Cu^{2+} was observed under three different experimental conditions (Figure 2). The results are summarized in Table 1. (a) When small pieces of the wire (6 $\phi \times 15$ mm) are placed separately on the paper (37 mm × 20 mm) (Figure 2a), the magnetic field does not affect the relative yield of Cu^{2+}. (b) When a copper wire (6 $\phi \times 250$ mm) is placed on the three pieces of paper, placed separately as depicted in Figure 2b, the magnetic field does not affect the yield of Cu^{2+}. (c) Only when the long piece (37 mm × 300 mm) of paper is used (Figure 2c) does the yield

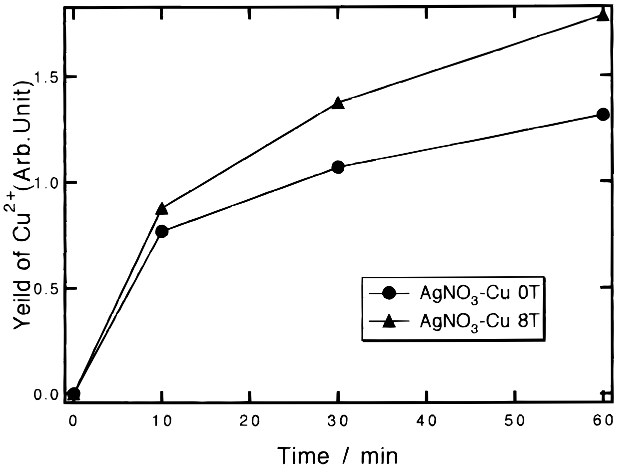

Figure 7. Relative yields of copper ions vs time for the Ag^+/Cu reaction in the absence and presence of a magnetic field ($B_{max} = 8$ T).

increase at the high magnetic field region ($z = 0$ mm), whereas it decreases at the low magnetic field region ($z = 115$ mm).

3.4. Electromotive Force. The present redox reaction in the gradient magnetic field generates an electromotive force. It was measured using the experimental setup depicted in Figure 3. Two sets of copper wire (6 $\phi \times 50$ mm × 4) are placed at the positions of $z = 0$ and $z = 125$ mm on a piece of chromatography paper wet with silver nitrate aqueous solution. The results are shown in Figure 8. In the absence of a magnetic field no electromotive force is generated. When a magnetic

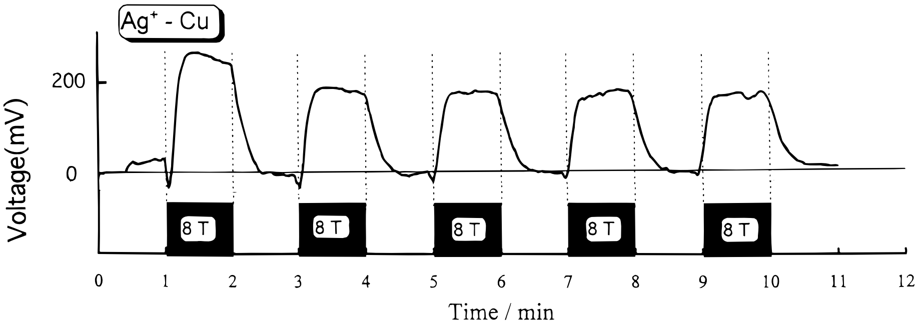

Figure 8. Electromotive force for the Ag^+/Cu redox reaction induced by a magnetic field ($B_{max} = 8$ T). A closed box around "8 T" indicates the time period when the reaction system is exposed to the magnetic field. Unless otherwise noted, the reaction is carried out at zero field. Experimental setup is given in Figure 3.

TABLE 1: Influence of the Size of the Paper and Copper Wire on the Relative Yields Φ(8 T)/Φ(0 T) of Copper Ion. Φ(8 T) and Φ(0 T) Are the Yields in the Presence and Absence of a Magnetic Field ($B_{max} = 8$ T). For Experimental Setup, See Figure 2

z/mm $B(z)$/T	0 8	50 6.6	115 2.6
case a	0.98	0.95	0.92
case b	1.02	1.07	0.92
case c	1.63	1.43	0.46

field ($B_{max} = 8$ T) is applied, an electromotive force of ca. 200 mV is generated between the two sets of identical wire.

The electromotive force for the Ag^+/Zn redox reaction was also examined. The force for this reaction is less than 20 mV under the analogous condition. The electromotive force generated from the Ag^+/Zn reaction is insignificant, as compared with that generated from the Ag^+/Cu reaction.

4. Discussion

Now let us consider the mechanism of MFEs mentioned above. In general there are three mechanisms to explain the observed effects. (a) The first is the difference in the Gibbs free energies in the magnetic fields,[2] (b) the second is the magnetohydrodynamics (MHD) mechanism,[8] and (c) the third is the magnetic force caused by a gradient magnetic field (*magnetophoresis*).[13]

The Gibbs free energy change ΔG for reaction 2, which is induced by a magnetic field, is

$$\Delta G = (-1/2\mu_0)\Delta\chi V B(z)^2 \qquad (5)$$

where $\Delta\chi$ is the difference between magnetic susceptibilities χ of ions and metals of eq 2, and V and μ_0 are the volume of the sample and magnetic permeability, respectively. $B(z)$ is the magnetic field strength at the position z. The difference in the Gibbs free energy ΔG at the center and edge of the wire may induce a shift of chemical equilibrium of the redox reaction. By assuming that molar magnetic susceptibilities of copper, copper ion, silver, and silver ion are $-4\pi \times 5.46 \times 10^{-12}$, $+4\pi \times 1.28 \times 10^{-9}$, $-4\pi \times 2.05 \times 10^{-11}$, and $-4\pi \times 2.4 \times 10^{-11}$ m^3 mol^{-1} (all values are described using SI units), respectively, and magnetic fields at the center and the edge of the wire are 8 and 2 T, respectively, ΔG's are estimated to be -1.04×10^{-1} at 8 T and -6.47×10^{-3} J at 2 T, respectively, when all silver ions (0.5 mol dm^{-3}) react with copper metal (0.25 mol dm^{-3}). Thus, the difference in free energy change between the center and the edge of the wire is -9.8×10^{-2} J. This free energy difference is too small to explain the MFE shown in Figures 4 and 5. As shown in Table 1, the yield of copper ion is independent from the magnetic field when the reaction is carried out on a small piece of separate paper. Furthermore, the electromotive force between the two sets of copper wire shown in Figure 3 is estimated to be 2.0×10^{-6} V from the above-mentioned free energy difference. This value is too small to explain the observed electromotive force (ca. 200 mV) shown in Figure 8.

The MHD force $\boldsymbol{F}_{MHD}$ is given by the following equation:

$$\boldsymbol{F}_{MHD} = e\boldsymbol{v} \times \boldsymbol{B} \qquad (6)$$

where e is the electric charge, $\boldsymbol{v}$ is its velocity, and $\boldsymbol{B}$ is the homogeneous magnetic field. The MHD force $\boldsymbol{F}_{MHD}$ gives charged species torque perpendicular to both $\boldsymbol{v}$- and $\boldsymbol{B}$-axes. When $\boldsymbol{v}$ and $\boldsymbol{B}$ are perpendicular to each other, $\boldsymbol{F}_{MHD}$ is maximum, whereas $\boldsymbol{F}_{MHD}$ is zero when $\boldsymbol{v}$ and $\boldsymbol{B}$ are parallel. Mogi et al. have reported that a high magnetic field affects the deposition pattern of this Ag^+/Cu redox reaction.[8] In their experiment, the direction of the magnetic field is perpendicular to the motion of ions. In the present experiment, the direction of the flow of ions is parallel to that of the magnetic field as a whole. It might also be possible to consider that the flow in the vicinity of the wire might take an important role in the MFEs. In this case, the flow is considered to be perpendicular to the magnetic field from the dendritic pattern at zero field shown in Figure 4. Under this circumstance, the force is perpendicular to the surface of the paper, and therefore, the MHD force does not induce a convective flow in the present redox reactions. Furthermore, the Ag^+/Zn reaction should be affected by the external magnetic field, if the MHD mechanism is operative. Contrary to this prediction, the magnetic field does not affect the dendritic pattern deposited from the Ag^+/Zn redox reaction (Figure 6). Therefore, the MHD mechanism does not explain the experimental results shown in Figures 4 and 5.

Magnetic properties of reactions 2 and 3 are different from that of reaction 4. In reaction 2, diamagnetic reactants (Ag^+ and Cu) generate a paramagnetic product (Cu^{2+}), and in reaction 3, a paramagnetic reactant (Cu^{2+}) changes into a diamagnetic product (Cu). In reaction 4, which does not exhibit MFEs, both reactants and products are diamagnetic. Thus it is reasonable to consider that the MFEs observed in reaction 2 are associated with the paramagnetic property of the product (Cu^{2+}). Furthermore, as shown in Table 1, the redox reaction carried out on a small piece of paper exhibits no MFE (cases a and b). In these cases, the difference in the magnetic field strengths ΔB at the two ends of the wire is small and the reaction is considered to be carried out in a locally homogeneous magnetic field. In case c, which exhibits significant MFEs, ΔB between the center and edge of the wire is about 6 T, and therefore, the reaction is carried out under a high gradient magnetic field as a whole. Since not a homogeneous field but a gradient one affects reaction 2, the magnetic force is considered to be operative in the MFEs shown in Figures 4 and 5.

The magnetic force F_{GMF} induced by the gradient magnetic field is given by

$$\boldsymbol{F}_{\mathrm{GMF}} = (\chi/\mu_0)B(z)\,\mathrm{d}B(z)/\mathrm{d}z \qquad (7)$$

Silver ion and water are diamagnetic, whereas copper ion is paramagnetic. Silver ion and water are repelled by the gradient field, whereas copper ion is attracted by the field. Suppose the maximum value of magnetic field $B(z)(\mathrm{d}B(z)/\mathrm{d}z)$ is estimated to be ca. 380 $\mathrm{T}^2\ \mathrm{m}^{-1}$ ($z = 50$ mm, see Figure 1), the magnetic force for a 0.25 mol dm^{-3} aqueous solution of Cu^{2+} is estimated to be 1.2 N dm^{-3}, whereas that for a 0.5 mol dm^{-3} solution of Ag^+ is estimated to be -4.6×10^{-2} N dm^{-3}. The force for the Cu^{2+} solution is about 1/8 of gravity. Thus, the paramagnetic copper ion is the key compound for the MFEs shown in Figures 4 and 5. As shown in Table 1, significant MFEs are observed only when the copper wire is placed on a long sheet of paper. This is a strong piece of evidence that a convective flow of the solution is induced along the z-axis by the gradient magnetic field. Neither conduction of electric current in the wire nor the Gibbs free energy difference takes an important role in the MFEs.

It is considered that the surface of chromatography paper wet with aqueous solution is covered with a thin layer of the solution. In the absence of the magnetic field the liquid–solid redox reaction is diffusion-controlled. When it is carried out in the high gradient field, it is allowed to suffer from the magnetic-field-induced convection as the reaction time proceeds. This is because the concentration of paramagnetic copper ion in solution increases upon the reaction. The MFEs shown in Figures 4 and 5 are explained as follows: (1) Before the reaction, the aqueous solution is diamagnetic. At the initial stage of the reaction, the copper ion is generated uniformly in the vicinity of the copper wire. (2) When the concentration of copper ion becomes higher, the solution in the vicinity of the wire becomes paramagnetic as a whole and then it starts to move to the higher gradient field. This induces convection of solution on the surface of the chromatography paper. Because of this convection, mass transfer to the front of the reaction area (copper metal surface and silver dendrite) is enhanced. This results in the change in deposition pattern of the dendrite as well as the increase in the reaction yields in the presence of the gradient magnetic field. From the magnetic susceptibilities of water and ions, the solution in the vicinity of the copper wire is considered to become paramagnetic when the local concentration of copper ion becomes higher than ca. 0.6 M. It must be pointed out that a homogeneous solution composed of paramagnetic and diamagnetic compounds receives a magnetic force proportional to the sum of magnetic susceptibilities of components. In a homogeneous solution each component does not move independently in the magnetic field.

The electromotive force (emf) generated from the Ag^+/Cu redox reaction shown in Figure 8, then, may be explained by the convection of a solution on the surface of the chromatography paper, since no remarkable emf is generated in the Ag^+/Zn reaction where both reactants and products are diamagnetic. There are two possibilities of the effect of convection on the generation of the emf. (1) The convection induces a concentration differencce between the two sets of copper wire, resulting in the formation of a concentration cell. (2) The convective flow between the two sets of wire induces the emf.

In case 1, the emf of the concentration cell, E, is given by the equation[14]

$$E = -(RT/F)\ln(m_1/m_2) \qquad (8)$$

where R is the gas constant, T is the temperature, F is the Faraday constant, and m_1 and m_2 are the concentrations of the solution at the electrode 1 and 2, respectively. As shown in Figure 8, E is ca. 200 mV in the present system. From eq 8, the concentration ratio m_1/m_2 is estimated to be ca. 2400. This value seems too large to explain the MFEs shown in Figures 4, 5, and 7. If this is the case, the observed MFEs should be very significant. Therefore, it is unlikely that magnetic-field-induced convection results in a concentration cell. In case 2, the observed emf may be explained as follows: In the presence of a high gradient magnetic field, the solution in the vicinity of the two sets of wire flows from the low field (2 T) to the high field (8 T), since it receives attractive force from the gradient field. This convection of a paramagnetic solution generates the emf in the gradient magnetic field. In Figure 8, upon application of the magnetic field, the voltage increases up to its maximum value with a time constant of ca. 10 s. This time constant seems to reflect a time by which the convective flow reaches a steady state. The induced electric current is estimated to be about 4×10^{-6} A, since the emf is about 200 mV and the impedance between the two sets of wire is about 50 kΩ. This corresponds to a flow of 1.5×10^{-7} mol of positive ions per 1 h. If the electric charge of Ag^+ is the origin of the electric current, this value corresponds to a flow of 1.6×10^{-5} g of Ag^+ per 1 h. Since, in the experiment shown in Figure 4, the amount of the deposited Ag metal is $(5-7) \times 10^{-2}$ g after 1 h of reaction, a flow rate of 1.6×10^{-6} g h^{-1} of Ag^+ between the two sets of copper wire seems attainable under the experimental condition shown in Figure 3. Thus, it is conceivable that the convective flow generates directly the emf shown in Figure 8.

In conclusion, the MFEs on silver metal deposition from the Ag^+/Cu redox reaction are attributable chiefly to the convection of solution which is induced by the magnetic force upon paramagnetic copper ions generated in the reaction.

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