3D-Morphological Chirality Induction in Zinc Silicate Membrane Tube Using a High Magnetic Field

Ichiro Uechi,[†,‡] Akio Katsuki,[§] Lev Dunin-Barkovskiy,[†] and Yoshifumi Tanimoto*[,†]

Institute for Molecular Science, Okazaki 444-8585, Japan, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan, and Faculty of Education, Shinshu University, Nagano 380-8544, Japan

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We report three-dimensional morphological chirality induction using a magnetic field. A right- or left-handed circular helix of zinc silicate membrane tube is selectively formed by application of a magnetic field (5−15 T), whereas the tube grows straight upward at zero field. Square and triangular helixes are also prepared. The results are interpreted in terms of the boundary-assisted magnetohydrodynamics mechanism in which the Lorentz force on ions in solution results in one-way convection of the solution near the boundary.

1. Introduction

Chirality in nature is of great interest for many scientists,[1] since it would be related to origin of life. For many years, magnetic field has been repeatedly discussed as a plausible cause of chirality in nature.[2,3] As for molecular chirality, recently Rikken and Raupach[4] have verified experimentally this possibility: in the photochemical reaction of Cr(III)tris-oxalato complex, the enantiomeric excess of its photoproduct is increased by ca. 1.5×10^{-4} by application of an external magnetic field of 15 T. Obviously it is very difficult to induce the molecular chirality with high efficiency, even though the induction is experimentally capable. Another type of chirality which is also seen in nature is a morphological one. Woodbine, for example, is tangled helically with a tree in a left-handed direction, whereas some other plant in a right-handed one. However, what determines their handedness is not unraveled. Therefore it is very interesting to examine whether a magnetic field can induce morphological chirality or not. Two-dimensional chirality induction using a magnetic field has been reported by Okubo and his collaborators.[5] They showed the leaves of silver dendrites, which are formed by the reaction of silver ion and a copper metal plate in aqueous solution, are tilted slightly in a right- or left-handed direction, depending on the direction of the magnetic field. The results are interpreted in terms of the Lorentz force on ions in the solution.

In this paper we report, for the first time, three-dimensional morphological chirality induction in a zinc silicate membrane tube, which would be called an artificial vine, by using a magnetic field. A right- or left-handed circular helix of the tube is formed *selectively* by application of a magnetic field of 5−15 T, whereas the tube grows straight upward at zero field. Square and triangular helixes are also prepared by slightly changing experimental condition. The results are interpreted in terms of the boundary-assisted magnetohydrodynamics (boundary-assisted MHD) mechanism in which the Lorentz force on ions in solution results in one-way convection of the solution near the boundary because of the steric condition posed by it.

* Author to whom correspondence should be addressed. E-mail: tanimoto@ims.ac.jp.
[†] Institute for Molecular Science.
[‡] Hiroshima University.
[§] Shinshu University.

2. Experimental Section

Magnetic fields were applied by using a superconducting magnet (JASTEC, JMTD-LH15T40).[6] The inner diameter of the room-temperature bore tube was 40 mm. The maximum field was 15 T, and the direction of the field was vertical and upward.

Zinc sulfate heptahydrate (Wako, 99.9%) and sodium silicate solution (Wako, 52−57%) were used as supplied. Distilled and deionized water was used. Typically, in a glass vessel (inner diameter 6 mm × length 50 mm) containing a small amount of zinc sulfate salt (ca. 0.2 g), a sodium silicate aqueous solution (relative density, 1.06) was slowly poured. The vessels were placed in the bore tube of the magnet and the outside of the magnet (leak field, ca. 2 mT). For the purpose of simplicity, the leak field of ca. 2 mT was called zero field. Several magnetic fields were applied to the vessels by placing them at different positions in the bore tube and therefore the fields are inhomogeneous.[6] After the reaction was carried out for 50−60 min in the bore tube, the vessels were taken out from the tube and the morphologies of the membrane were recorded by a conventional digital camera. All experiments were carried out at room temperature.

3. Results and Discussion

The reaction of metal salt crystal and sodium silicate aqueous solution is well-known as the "Silicate Garden Reaction",[7−9] which is the most interesting example of pattern formation reaction and has fascinated even a high school student for a long time. The mechanism of silicate garden reaction is complex, as briefly described below. When a metal salt crystal is added into a sodium silicate aqueous solution, a colloidal semipermeable membrane of metal silicate is formed on the crystal surface. Water diffuses osmotically into the space between the membrane and the crystal surface and dissolves the metal salt. As a result of this osmotic inflow of water, the membrane is ruptured and the solution rich with metal ions flows out. Then the metal ions in the outflow react with silicate ions outside of the membrane, forming hollow tubes. Because of the difference in density of the aqueous solutions outside and inside the membrane, hollow tubes grow upward. In this study, diamagnetic zinc sulfate is chosen as the crystal. The reaction of zinc silicate membrane formation in a sodium silicate aqueous

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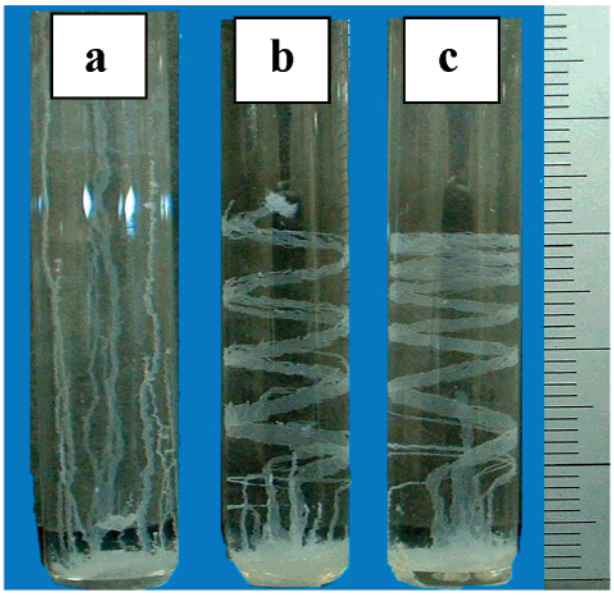

Figure 1. Photographs of the zinc silicate membrane tubes in magnetic field. (a) Zero field, (b) $B_{mean} = 6$ T, (c) $B_{mean} = 13.5$ T. Here the mean magnetic field, B_{mean}, was obtained by averaging the intensities at the start and end points of the membrane grown in a magnetic field, as the fields are inhomogeneous. The small unit on the scale is 1 mm.

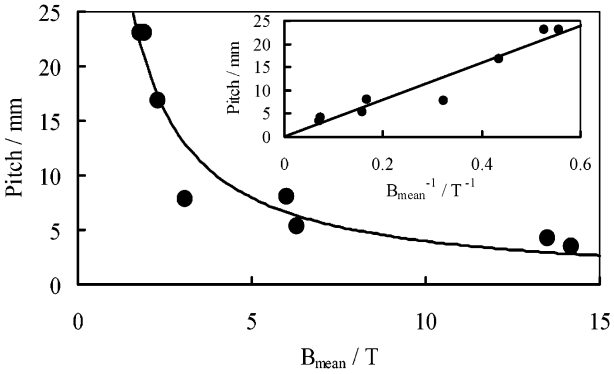

Figure 2. Plot of mean pitch, p, of the membrane helix vs mean magnetic field, B_{mean}. The inset shows plot of p vs $1/B_{mean}$. The mean pitch, p, was obtained by averaging all individual pitches between the start and end points of the membrane grown in a glass tube in magnetic fields, as the fields are inhomogeneous. Solid lines in the figure are simulated ones by assuming a linear relationship between p and $1/B_{mean}$.

solution (pH $\sim$ 12) is given symbolically as follows:[10,11]

$$[SiO_4]^{4-} + 2Zn^{2+} \rightarrow Zn_2SiO_4\downarrow \qquad (1)$$

Figure 1 shows magnetic field effects (MFEs) on the growth of zinc silicate membrane tubes. Cylindrical glass vessels containing zinc sulfate crystals and a sodium silicate solution are placed at zero field for 5 min and then in each magnetic field for 55 min. At zero field, the tubular membrane grows almost vertically upward. In the presence of magnetic fields, the tubes or bundles of the tube grow *helically* upward. Chirality of the helixes is always right-handed. An external magnetic field changes the three-dimensional morphology of the tube dramatically. Figure 2 shows the MFE on the pitch, p, of the helical tubes. Here the mean magnetic field, B_{mean}, is obtained by averaging the intensities at the starting and end points of the membrane grown in a magnetic field and the mean pitch is obtained by averaging all individual pitches between the two points in the vessel, as the field is inhomogeneous. The pitch decreases with increasing magnetic field. In addition, the length of the tube at 14 T is 2−3 times longer than that at zero field. The pitch of helical tubes decreases with increasing the magnetic field, whereas the growth rate of the tube increases significantly in magnetic fields.

There are several mechanisms of MFEs on chemical and physical processes.[12,13] In the present case, the reaction is localized at the front of membrane tube and the transportation of ions from the bulk solution to the front would be the rate-determining step, indicating that the transportation of ions in solution would be affected by either the Lorentz force or the magnetic force. The influence of magnetic force, however, would be negligible in the present reaction, though it is carried out in inhomogeneous magnetic field. This is because only diamagnetic ions are involved in the reaction and because the direction of the magnetic force, which is parallel or antiparallel to the magnetic field, cannot induce circumferential motion of ions at all. The present helix formation can be explained in terms of the MHD mechanism where the Lorentz force on the motion of ions moving thermally in the solution induces one-way convection of the solution. The Lorentz force ($\boldsymbol{F}_L$) is given by the following equation,

$$\boldsymbol{F}_L = e\boldsymbol{v} \times \boldsymbol{B} \qquad (2)$$

where e is the electric charge of an ion, $\boldsymbol{v}$ is its velocity, and $\boldsymbol{B}$ is the magnetic field intensity. Ions moving perpendicular to the magnetic field receive torque due to the Lorentz force.

The length of tubular membranes increases with the magnetic field, as the convection is enhanced by the magnetic field. Furthermore, if the Lorentz force could induce helical growth of a zinc silicate membrane tube, the pitch of the helix would be affected by the force. The pitch, p, is expected to decrease inversely with increasing the magnetic field, since it is proportional to the ratio of the rate of the vertical motion of ions, which determines the vertical growth rate of the membrane and is magnetic-field independent, and that of the circumferential motion of ions induced by the Lorentz force. As shown in the inset of Figure 2, there is a good linear relationship between p and $1/B_{mean}$, indicating that the Lorentz force is responsible for the helical growth of the membrane.

Now let us consider the mechanism of the helical growth of the membrane tube in detail. There are two questions to be answered. The first is why the Lorentz force induces the helical growth. The second is which ion is the main cause of this phenomenon, as the present solution is composed of positive ions (Na^+, Zn^{2+}), negative ions (SiO_4^{4-}, SO_4^{2-}), and neutral water molecules. Figure 3 shows a schematic model for the helical growth of the zinc silicate membrane tube. Here, motions of negative ions in a magnetic field are depicted for the purpose of simplicity. Ions undergo cyclotron motion in a magnetic field. It is isotropic in average in a bulk solution, since ions move randomly in all directions, resulting in isotropic growth of the membrane tube. On the other hand, ions near the vessel wall bounce on the wall to the inner radial direction and, therefore, the motion of these ions is anisotropic. This anisotropic motion of ions results in the one-way convection of the solution near the wall, since in aqueous solution collision of ions and molecules is so frequent that individual ions cannot move independently but all ions and molecules move collectively. Then, which ion is the main cause of the present convection? Helical growth is mainly observed for membrane tubes growing near the vessel wall. This means that the ions moving near the wall, i.e., Na^+ or SiO_4^{4-}, are chiefly responsible to the present phenomenon. Zn^{2+} and SO_4^{2-} ions cannot be the main cause, since they are located inside of the membrane tube where

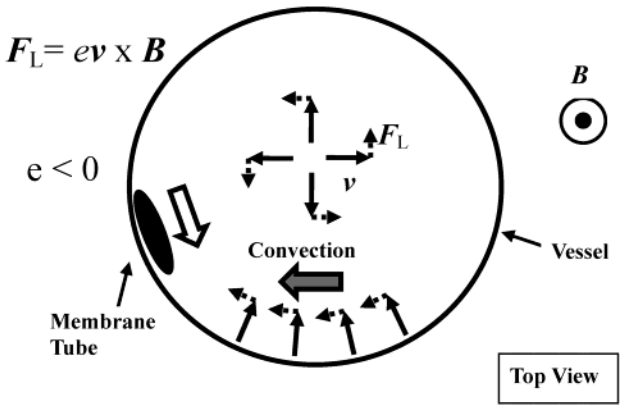

Figure 3. Schematic model for helical growth of zinc silicate membrane tube in a magnetic field (top view). Motions of negative ions and the direction of the Lorentz force on them are depicted by full and dashed line arrowheads. The direction of the magnetic field is perpendicular to the paper and upward.

influence of the vessel wall is very small. However, it is very hard to clarify which of Na^+ or SiO_4^{4-} is the cause of the convection at the present stage of study. From the computer simulation study of morphological evolution of the diffusion-limited aggregation under rotating flow, it is shown that the aggregation grows to the upstream direction.[14] Magnetic field effects on the patterns of copper and silver dendrites are also explained by the upstream growth of their dendrites.[15] By analogy, it seems most reasonable that the front of the tube, which is filled with concentrated Zn^{2+} solution, grows to the direction where fresh and concentrated SiO_4^{4-} ions are supplied not only by diffusion but also by convection. Downstream growth of the tube might be another possible mechanism. However this possibility would be low, since the convection induced by the magnetic field seems too weak to distort the front of the tube (vide infra). Thus, the membrane tube might grow to the upstream direction. If this is the case, the direction of the convection is left-handed, as that of tube growth is right-handed. This consideration means that the Lorentz force on SiO_4^{4-} negative ions is the cause of the one-way convection, though its rate could be reduced in a great extent due to the opposite motion of Na^+ positive ions. In the case of silver dendrite reaction, in-situ observation of the dendrite growth in a magnetic field has revealed that the solution near the top of the dendrite undergoes the magnetic field-induced convection,[16] as predicted by the current model.

For an order of magnitude estimate, the Lorentz force on silicate ion is calculated using the diffusion coefficient of the ion. The relationship of the diffusion coefficient, D, the jumping length, λ, and the jumping time, τ, of an ion in solution is given by the Einstein−Smoluchowski equation,[17]

$$D = \lambda^2/2\tau \tag{3}$$

Then the mean velocity of the ion is given as λ/τ, as λ and τ refer to the mean free path and its time of the ion, respectively, assuming that the solution is the perfect gas. Putting this value in eq 2, we obtain

$$F_L = e(\lambda/\tau)B \tag{4}$$

when the ion moves in the plane perpendicular to the magnetic field. D for silicate ion is assumed to be 1×10^{-5} cm^2 s^{-1} which is the value for SO_4^{2-}, since D for silicate ion is unknown. λ is assumed to be 150 pm which is the diameter of a water molecule, as collision of the ion with water would occur when

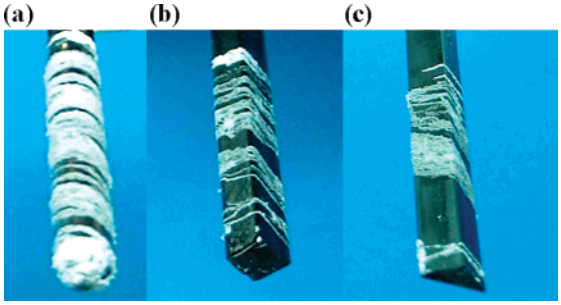

Figure 4. Photographs of zinc silicate membrane helixes grown at $B_{mean} = 14.2$ T in the presence of (a) a 2-mm glass rod, (b) a 3-mm square plastic bar, and (c) a 3-mm triangular plastic bar, at the center of the glass vessel.

it moves in the length of a water diameter. Then, λ/τ is calculated to be 14.7 m s^{-1}. F_L is 5.7×10^7 N mol^{-1} at 10 T. The force on the solution studied here is 2.9×10^7 N dm^{-3}, since its concentration is about 0.5 mol dm^{-3}. The average force must be zero in the absence of vessel wall, since the motion of the ions is random, and therefore the forces are canceled out. On the vessel wall, however, the ions bounce to the inner radial direction, resulting in the unidirectional Lorentz force. In the solution studied here, Na^+ and SiO_4^{4-} ions coexist. When the force on Na^+ is not rigorously equal to that on SiO_4^{4-}, then the residual anisotropic force would induce convection of the solution near the wall, even though it is several orders of magnitude smaller. This is because the unidirectional magnetic force of 1.2 N dm^{-3} can induce convection of a solution in the case of silver dendrite formation reaction.[13]

If the above consideration is correct, it could be possible to prepare the left-handed helical membrane tube by simply exchanging the relative orientation of the wall and the bulk solution in a glass vessel. To confirm this possibility, a glass rod of 2-mm outer diameter is placed at the center of the vessel in the solution. In this case, the convection of the solution near the glass rod surface would be right-handed, resulting in the formation of the left-handed helical membrane tubes. The result is given in Figure 4a. As expected, left-handed helixes of the membrane tube are grown on the wall of the glass rod. Furthermore, to examine the influence of shape of the rod, square and triangular plastic bars are placed in stead of the glass rod. As shown in Figure 4b,c, square and triangular helixes of the membrane tube are obtained. In the case of the triangular bar where the two edge angles are as sharp as 45°, the tube grows precisely on the surface by turning its direction by 315° at the two edges. The shape of the helixes is the accurate reflection of that of the rod, the convection induced by the magnetic field being quite weak. This fact also supports the importance of the boundary condition in the helix formation of the membrane tube. Therefore, it is concluded that the wall of the vessel or the rod is essential for inducing the one-way convection of the solution by the Lorentz force. Although a left-handed helix would be obtained simply by changing the magnetic field direction, we could not perform this experiment because of the protection circuit of the magnet.

Two-dimensional chirality induction using a magnetic field has been reported by Okubo and his collaborators.[5] They studied the reaction of silver ion and copper metal plate in aqueous solution in a dish,

$$2Ag^+ + Cu \rightarrow 2Ag\downarrow + Cu^{2+} \tag{5}$$

Growth pattern of silver dendrites is spiral appreciably but

slightly, when a vertical magnetic field of 4 T is applied. The spiral direction depends on that of magnetic field. The results are interpreted in terms of the Lorentz force on ions moving in the solution. In the present case, the chirality is 3-dimensional and morphological change which is induced by the magnetic field is very significant compared to that of the silver dendrite. As pointed out, the morphological chirality is induced chiefly at the boundary of solid and liquid interfaces. In the present case, the boundary due to the wall of vessels is well-defined as membrane tubes grow upward and uniform and one-way motion of the ion is induced. On the contrary, in the case of silver dendrite, the motion of ions is controlled by the solid surface of copper plate only at the initial stage of the deposition and after growing dendrites it is controlled mainly by leaves of the dendrite which have complex surface structure and the motion of ions becomes nonuniform. This is why the change induced by the magnetic field is not significant in the case of the dendrites.

The present results would give a mechanism of morphological chirality induction in nature by a magnetic field. The boundary-assisted MHD mechanism is not special for the membrane tube growth but is always operative at the interface between an ionic solution and a solid surface. Therefore, this mechanism is of great importance in controlling the process, such as physical and chemical deposition of solids, occurring at the interface between the two phases. Crystals having minimal defects would be obtained by application of a magnetic field. In addition, influence of the wall would become significant when the diameter of a vessel decreases. If an ionic reaction could be carried out in a micro- or nanoscale reactor, such as holes of mesoporous silica, in the presence of a magnetic field, helical (and therefore chiral) molecules might be synthesized. This consideration would lead to a new hypothesis on the induction of helical (chiral) molecules.

4. Conclusion

In conclusion, we have succeeded to prepare selectively helixes of zinc silicate membrane hollow tubes with either right- or left-handed morphology using a vertical magnetic field. Although the Lorentz force itself could not induce one-way convection of the solution at all, this happens with the aid of the wall of the vessel near which motion of ions becomes one-direction (boundary-assisted MHD mechanism). The salient feature of the present results is that the boundary condition imposed by the solid−liquid interface is extremely important to obtain the significant morphological chirality induction using a magnetic field. This study would also suggest a new model of morphological chirality induction and a new concept in controlling the chemical and physical process occurring at the interface between the ionic solution and solid surface, using a magnetic field.

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