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Effect of Vertical Magnetic Field on the Chemical Wave Propagation Speed in Belousov–Zhabotinsky Reaction

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Effects of a *vertical* magnetic field (maximum field, 4 T and 93 $T^2\,m^{-1}$) on chemical wave front propagation from the Belousov–Zhabotinsky reaction were studied. Applied magnetic fields strongly affected the downward propagation speed in a glass tube. The magnetic force acting on the inhomogeneous solution explains the results.

Magnetic fields affect various chemical and physical processes.[1] Especially, magnetic field effects (MFEs) on inhomogeneous chemical reaction are of great interest because, in inhomogeneous reactions, mass transport is a key process that a magnetic field can easily affect. Nevertheless, such examples are few.[2–4]

The Belousov–Zhabotinsky (BZ) reaction is well known as a model for biological phenomena.[5] The MFE on this reaction has been reported.[6,7] A magnetic field strongly affects a two-dimensional pattern generated by the reaction in a dish when the reaction is conducted on a pair of permanent magnets (maximum field, ca. 200 mT).

This study examines the effect of a *vertical* magnetic field (maximum field, 4 T and 93 $T^2\,m^{-1}$) on a *quasi-one-dimensional* chemical wave front propagation speed prepared using the BZ reaction as a new example of MFE on inhomogeneous reaction. Results show that the magnetic field strongly affects the propagation speed and that the magnetic force acting on the inhomogeneous solution explains MFE.

All chemicals (GR grade, Wako Pure Chemical Industries Ltd.) were used as received. Deionized and distilled water was used. Ferroin ($[Fe(phen)_3]^{2+}$) was prepared by mixing a stoichiometric amount of iron(II) sulfate and 1,10-phenanthroline. Stock solutions of malonic acid, sodium bromide, sodium bromate, ferroin, and sulfuric acid filtered using a membrane filter (0.43 μm) were mixed and let to stand for 3 min with occasional stirring. Their respective final concentrations were 0.1, 0.15, 0.03, 0.004, and 0.34 mol dm^{-3}. The mixed solution was filled into a glass tube (i.d. 2.6 mm × 180 mm). A silver wire (o.d., 2 mm) coated with organic paint and polished at the bottom end was inserted on the top of the solution. The tube was then installed in a bore tube of a superconducting magnet (SHI, HF5-50VHI-M2). Propagation of the chemical wave front was monitored from the side using a bore scope (R060-047-090-50, Olympus Corp.) with a CCD camera (OH-414, Olympus Corp.) and video recorder (GV-HD700, Sony Corp.). The propagation time of the room temperature reaction was measured from the position where the glass tube near the wave front was almost uniformly filled by the blue wave front solution: its steady propagation was achieved at zero field. For simplicity, the product of magnetic flux density (B) and its gradient ($\partial B/\partial z$) in the vertical direction (z) is designated as a magnetic force field. Changing the glass tube position in the magnet bore and changing the magnet's electric current varied the magnetic fields and magnetic force fields.

The reaction starts shortly after triggering by a silver wire. The solution near the bottom of the wire turns from red to blue because the solution used in this study is under an excitable condition. Then the blue wave front moves downward. Figure 1 portrays a plot of the wave front position vs. time in magnetic fields. From the slope of the plot, the propagation speed is obtained as 0.11 (0 T, 0 $T^2\,m^{-1}$), 0.27 (2.5 T, −93 $T^2\,m^{-1}$), 0.07 (2.5 T, +93 $T^2\,m^{-1}$), and 0.11 mm s^{-1} (4 T, 0 $T^2\,m^{-1}$). The speed at 2.5 T and −93 $T^2\,m^{-1}$ is about 2.5 times that at 0 T and 0 $T^2\,m^{-1}$, whereas the value at 2.5 T and +93 $T^2\,m^{-1}$ is about 0.6 times that at 0 T and 0 $T^2\,m^{-1}$. The speed at 4 T and 0 $T^2\,m^{-1}$ is practically equal to that at 0 T and 0 $T^2\,m^{-1}$. These facts indicate that not magnetic flux density (B) but the magnetic force field ($B(\partial B/\partial z)$) causes the MFE.

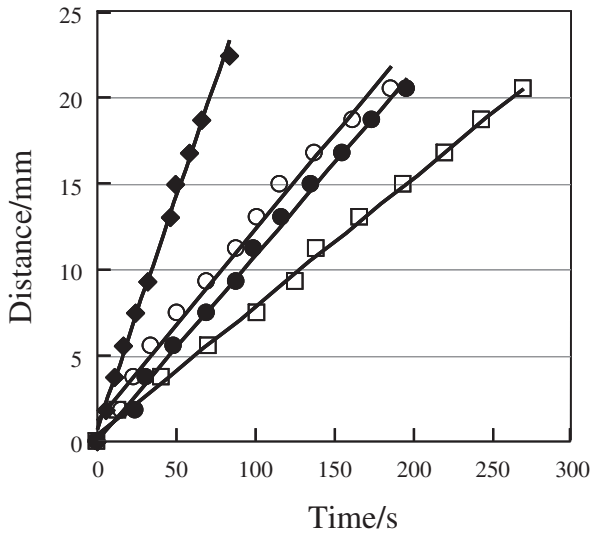

Figure 1. Plot of position of chemical wave front vs. time in magnetic fields. ●, 0 T, 0 $T^2\,m^{-1}$; ◆, 2.5 T, −93 $T^2\,m^{-1}$; □, 2.5 T, +93 $T^2\,m^{-1}$; and ○, 4 T, 0 $T^2\,m^{-1}$.

Figure 2 presents the magnetic force field dependence of the propagation speed. The speed is almost linearly increasing concomitantly with increasing magnetic force field in negative direction, although it decreases slightly with the increasing field in the positive direction.

The MFE on the wave front propagation speed is explainable by the magnetic force, F_{mag}, acting on the blue wave front solution.[1]

$$F_{mag} = (1/\mu_0)(\chi_b - \chi_r)B(\partial B/\partial z) \quad (1)$$

Therein, μ_0 is the magnetic permeability in vacuum, χ_b is the magnetic susceptibility of the blue wave front solution, and χ_r is that of red bulk solution. The direction of F_{mag} depends on the sign of the product of $(\chi_b - \chi_r)$ and $B(\partial B/\partial z)$. When the product sign is positive, the force is upward, but it is downward when the sign is negative. The results in Figures 1 and 2 show that the sign of $(\chi_b - \chi_r)$ is positive or $\chi_b > \chi_r$, as the speed increases by application of −93 $T^2\,m^{-1}$ and decreases by application of +93 $T^2\,m^{-1}$.

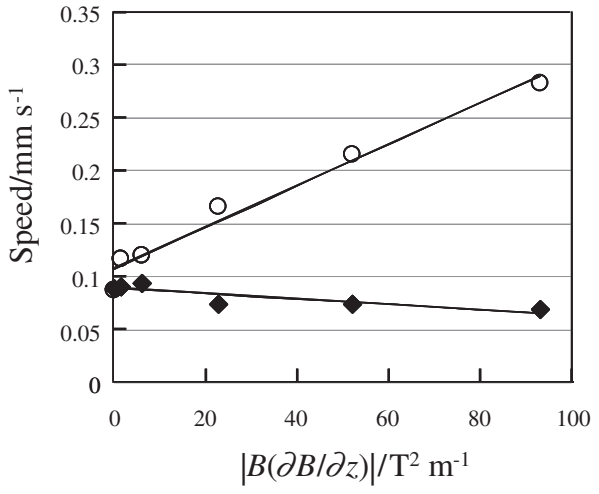

Figure 2. Influence of magnetic force field on the chemical wave front propagation speed. The sign of $B(\partial B/\partial z)$ is negative (○) and positive (◆).

This reaction, where ferroin is involved in the reaction as catalyst, is symbolically expressed as eq 2.

$$5HO_2CCH_2CO_2H + 3BrO_3^- + 3H^+ \rightarrow 3HO_2CCHBrCO_2H + 2HCO_2H + 4CO_2 + 5H_2O \quad (2)$$

The BZ reaction comprises more than 10 elementary steps and involves more than 10 chemical species including $BrO_2^\bullet$ radical. Ferroin (catalyst) is oxidized to ferriin in this reaction. Ferroin ($[Fe(phen)_3]^{2+}$) and ferriin ($[Fe(phen)_3]^{3+}$) are presumably diamagnetic and paramagnetic respectively, as $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are diamagnetic and paramagnetic, respectively.[8] The blue solution at the wave front is rich in ferriin (ferriin is blue), although the bulk solution contains the red ferroin. The condition $\chi_b > \chi_r$ is attainable because the blue wave front solution contains paramagnetic species such as ferriin, although it is impossible to identify uniquely which species is responsible for the change of χ by the chemical reaction.

For the purpose of an order estimation, the magnetic force on the 0.004 mol dm^{-3} solution of $K_3[Fe(CN)_6]$ ($\chi = 6.96 \times 10^{-6}$ cm^3 g^{-1})[9] in a $K_4[Fe(CN)_6]$ ($\chi = -0.374 \times 10^{-6}$ cm^3 g^{-1})[9] solution at 93 T^2 m^{-1} is calculated. It is about 900 dyn dm^{-3}. This value is very small. Nevertheless, the magnetic force of this intensity can induce solution convection, as a paramagnetic $FeCl_3$ solution in water is reported to drift toward a convensional permanent magnet surface.[10]

Figure 2 shows the asymmetric effect of magnetic force. The speed is proportional to the downward force field, although the upward field's influence is much smaller. This difference is explainable by the wave front shape (Figure 3). The wave front solution changes its shape in magnetic fields. It is flat with an unclear interface at 0 T^2 m^{-1}. It is parabolic at -93 T^2 m^{-1} and is flat with a distinct interface at $+93$ T^2 m^{-1}. This wave front shape change might be attributable to the difference in the moving speed of the front and the reaction speed. At -93 T^2 m^{-1}, the front solution is attracted downward and the solution moves quickly compared with the reaction rate. Therefore, no time exists to fill the tube full with the blue solution, indicating that there exists a vacancy to undergo the convection of the solution near the wave front. At $+93$ T^2 m^{-1}, the front solution is attracted upward and the propagation slows. Therefore, the tube near the reaction front is completely filled by the blue solution, indicating that no space exists for convection near the wave front.

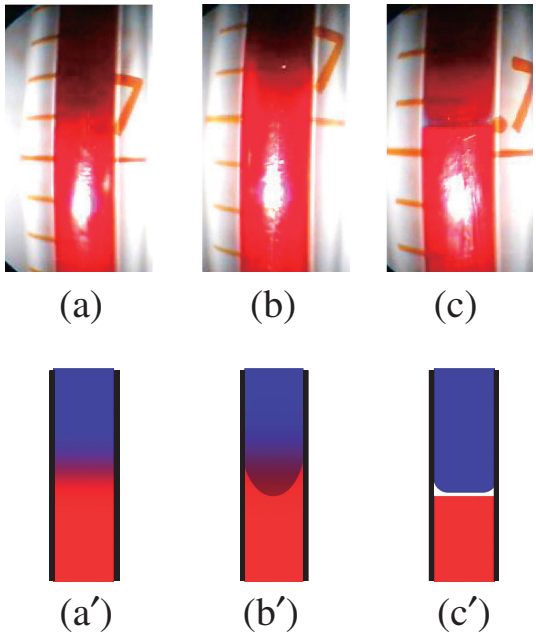

Figure 3. Shape of chemical wave front in magnetic fields. (a) 0 T, 0 T^2 m^{-1}; (b) 2.5 T, -93 T^2 m^{-1}; and (c) 2.5 T, $+93$ T^2 m^{-1}. (a′), (b′), and (c′) are respective schematics of (a), (b), and (c).

Influence of a tube size is examined using a large glass tube (i.d., 8 mm). At zero field, the blue solution formed at the bottom surface of a silver wire gradually spread in the tube with gradulally moving downward. At -93 T^2 m^{-1} the blue solution with mushroom shape moves downward quickly. At $+93$ T^2 m^{-1} the solution at bottom end of a silver wire moves upward to the surface of the solution, full fills the tube, and then moves downward slowly. These shape changes in magnetic fields strongly indicate that the solution convection takes place when an open space is available.

In the case of MFE on a two-dimensional pattern generated by the BZ reaction using a permanent magnet,[6,7] the propagation of the fastest wave front shows a sigmoid increase along the peak magnetic gradient line but not along the peak magnetic force product line. Present result clearly shows the MFE is attributable to the convection induced by the magnetic force. Probably in the former case, the magnetic field direction is three-dimensional and complex to estimate mechanism of the observed effect.

In conclusion, it is clarified that magnetic field effects on the wave front propagation speed are attributable to the magnetic force-induced convection near the the wave front solution.

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