In Situ Observation of Laser-Induced Convection of Water in High Magnetic Fields Using a Photochromic Reaction

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The effects of vertical magnetic fields on laser-induced convection of water were studied using a photochromic reaction of a water-soluble 1,2-diarylethene (WSD). A thin blue disk of its photoisomer (PI) solution was formed on the bottom surface; it moved upward when the WSD aqueous solution was irradiated using a 355 nm laser from the bottom of the vessel. The lift speeds of the PI solution were about 2.5 (11 T, $+1200\,T^2\,m^{-1}$), 1.2 (11 T, $-1500\,T^2\,m^{-1}$), and 1.6 mm min^{-1} (15 T, $-100\,T^2\,m^{-1}$). All results are described in terms of the magnetic force acting on the PI solution.

The Earth's gravity induces convection of liquid solutions. For example, electrode reactions[1] and dendrite formation reactions[2] occurring at liquid/solid interfaces are strongly affected by gravity. It is important to control convection of liquid solutions in chemistry and physics; however, it is extremely difficult to prepare an environment that is free from the Earth's gravity. Usually, a space laboratory must be used for this purpose. Recently, magnetic fields have been recognized as useful tools for controlling convection. Today, we can use a magnetic force that is comparable to earth's gravity, even in conventional chemical laboratories. The behavior of diamagnetic solutions in high magnetic fields has been reported.[3–6] Mogi et al.,[3] for example, studied magnetic field effects on the thermal convection of water using a hybrid magnet.

To examine the influence of magnetic fields on the transient behavior of convection, we used a photochemical reaction for visualizing thermal convection because, in many photochemical reactions, a solution's color changes according to photoproduct formation; simultaneously, the temperature of the photoproduct solution increases because of the photon energy. Therefore, one can instantaneously generate a hot solution with visible color. Using photochromic[7] and photo-imaging reactions,[8] we studied the influence of high vertical magnetic fields on fast dynamics of photo-induced convection of benzene as it is commonly used in organic chemistry.

In this study, we examined the effects of vertical magnetic field on laser-induced convection of water to clarify how magnetic fields affect the fast dynamics of convection because water is the most important solvent in life sciences. Here, a photochromic reaction of water-soluble 1,2-diarylethene (WSD), shown in Fig. 1, was used for illustrating thermal convection. The convection was remarkably affected by vertical magnetic fields. The results are discussed in terms of the magnetic force acting on the photoisomer (PI) solution.

Experimental

4,4′-[(3,3,4,4,5,5-Hexafluoro-1-cyclopentene-1,2-diyl)bis(5-methyl-4,2-thiophenediyl)]bis[1-methylpyridinium] diiodide (WSD)

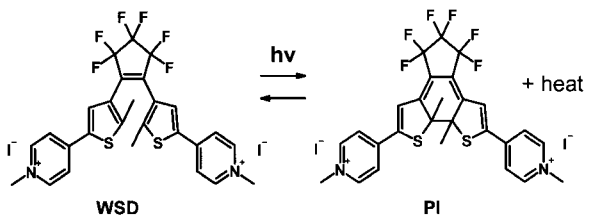

Fig. 1. Photoisomerization of WSD.

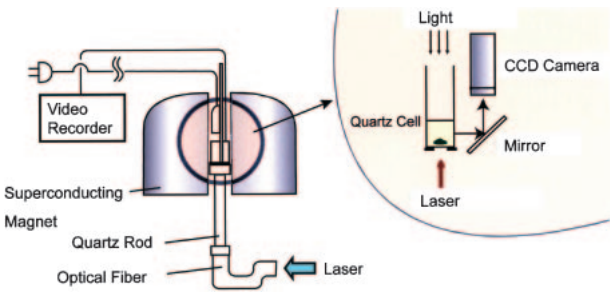

Fig. 2. Experimental setup (side view).

was synthesized as reported elsewhere.[9] Purified water (Wako Pure Chemical Industries Ltd.) was used as received. The concentration of WSD in water was about 3.1×10^{-4} mol dm^{-3}.

In situ observation of laser-induced convection in magnetic fields was carried out using the experimental setup shown in Fig. 2. A quartz cell (10 mm × 10 mm × 40 mm) containing a 0.001 dm^3 WSD aqueous solution was placed in a bore tube (φ 40 mm) of a superconducting magnet (LH15T40; Jastec Inc., vertical field). The solution was irradiated using single pulses (2.25 mJ) of 355 nm light from a Nd:YAG laser (INDI-40; Spectra-Physics, Newport Corp.) through a 6 mm hole from its bottom. The movement of the blue PI solution was observed using a CCD camera at a right angle and recorded using a video recorder. The movement of the forefront of the PI solution was analyzed using video software (Image J; Cosmos UI).

The experiments were carried out at three different positions in the bore tube: upper (11 T, $-1500\,T^2\,m^{-1}$), middle (15 T, -100

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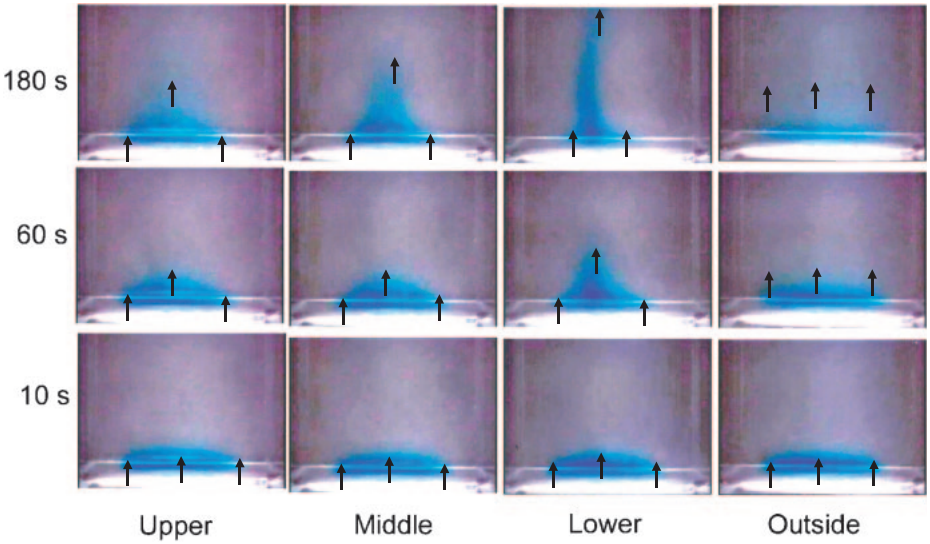

Fig. 3. Photo images of WSD aqueous solution after laser irradiation in magnetic fields (side view). Arrows indicate the position of the forefront of a blue PI solution. Horizontal: magnetic field condition—upper (11 T, $-1500\,T^2\,m^{-1}$), middle (15 T, $-100\,T^2\,m^{-1}$), lower (11 T, $+1200\,T^2\,m^{-1}$), and outside (0 T, $0\,T^2\,m^{-1}$). Vertical: delay time after laser irradiation.

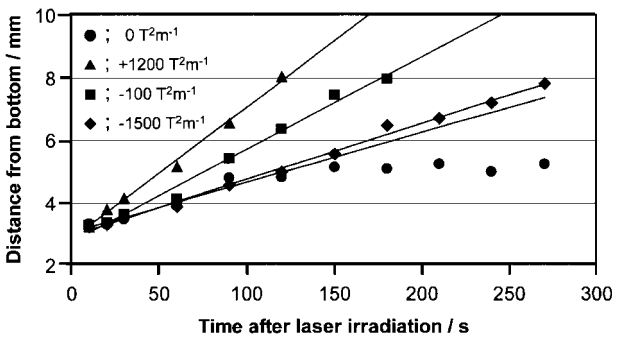

Fig. 4. Movements of forefront of the PI solution in magnetic fields. Abscissa: delay time after laser irradiation. Ordinate: distance of the forefront of a PI solution from the vessel bottom.

$T^2\,m^{-1}$), and lower positions (11 T, $+1200\,T^2\,m^{-1}$) and outside the magnet (0 T, $0\,T^2\,m^{-1}$) at room temperature.

Results

Figure 3 shows sequential photographs of the laser-irradiated WSD aqueous solution in magnetic fields. After laser irradiation, a thin disk of a WSD aqueous solution at the bottom of the cell became blue because of PI formation; the forefront of the blue solution then started to move upward. The movement of the blue solution in magnetic fields differed from that in a zero field. In a zero field, the forefront of the solution moved upward all together, retaining its shape. In magnetic fields, the forefront moved upward while centering to the radial center of the vessel.

Figure 4 shows the movement of the forefront of the PI solution in different magnetic fields. In a zero field, the solution moved upward slightly, then remained at that height after a delay time of 150 s. In magnetic fields, the forefront continued to move upward within a duration of about 250 s. From the initial slope of the plots shown in Fig. 4, the lift speeds of the forefront were calculated to be about 1.2 (0 T, $0\,T^2\,m^{-1}$), 1.2 (11 T, $-1500\,T^2\,m^{-1}$), 1.6 (15 T, $-100\,T^2\,m^{-1}$), and 2.5 mm min^{-1} (11 T, $+1200\,T^2\,m^{-1}$), with ±20% errors. Photo-induced thermal convection was enhanced when a $+1200\,T^2\,m^{-1}$ field was applied.

Discussion

Using laser irradiation, the photon energy absorbed by a WSD solution was partially used to induce the isomerization reaction of WSD to PI and the rest to heat the PI solution (Fig. 1). As a result, the density and magnetic susceptibility of the solution changed upon laser irradiation. In a zero field, the photo-generated PI solution moved upward because its density was less than that of the bulk solution. As it moves upward, it cooled by exchanging its thermal energy with the surrounding bulk solution and by mixing with the bulk solution. Finally, the temperature of the PI solution became equivalent to the temperature of the bulk solution, halting the PI solution movement. For that reason, the solution remained at the same height after 150 s in a zero field. In magnetic fields, an additional force acted on the solution. Magnetic force, which arises from magnetic susceptibility changes, influenced the movement of the PI solution, as discussed below. Contribution from a Lorentz force to convection was negligible, if any. It is because Lorentz force induces circular motion of ions in the plane perpendicular to both the moving direction of ions and a magnetic field and the colored solution moved mainly upwards, parallel to the magnetic field direction, as shown in Fig. 3.

With regard to this experiment, the temperature in the bore tube was slightly non-uniform in the radial direction because the lack of space (ϕ 40 mm) prohibited installation of a thermostat in the tube. The temperature at the bore-tube surface was about 2 K lower than room temperature. As a result, the solution near the inner surface of the cell was slightly lower in temperature than that near the center of the cell under the present experimental conditions, even though the solution volume was as small as 0.001 dm^3. The thermal convection attrib-

Table 1. Buoyancy and Magnetic Forces Acting on a PI Solution in Magnetic Fields

$B\partial B/\partial z$ /$T^2\,m^{-1}$	$\Delta\rho_{solution}g$ /$10^{-2}\,N\,m^{-3}$	$\Delta\chi_{H2O}B\partial B/\partial z$ /$10^{-2}\,N\,m^{-3}$	$(\chi_{PI}-\chi_{WSD})cB\partial B/\partial z$ /$10^{-2}\,N\,m^{-3}$	ΔF /$10^{-2}\,N\,m^{-3}$
0	7.6	0	0	7.6
+1200	7.6	3.6	−0.5	10.7
−100	7.6	−0.3	0.0	7.3
−1500	7.6	−4.5	0.6	3.7

uted to its non-uniform radial temperature distribution, whereby the solution near the vessel wall moves downward and that near the center moves upward, was induced in the solution placed in the bore tube. For that reason, the shape of the PI solution in magnetic fields differed from that in a zero field (outside of the magnet), and the speed at $-100\,T^2\,m^{-1}$ (1.6 mm min^{-1}) was slightly higher than that in a zero field (1.2 mm min^{-1}). The convection due to the non-uniform radial temperature distribution in the solution could not be neglected in the present study because the laser-induced temperature change was very small. Therefore, the lift speed of the PI solution at $-100\,T^2\,m^{-1}$ was the sum of the laser-induced thermal convection and the convection due to its non-uniform radial temperature distribution. In other words, it is the speed under a feeble magnetic gradient. Consequently, the lift speed under a feeble magnetic gradient was 1.6 mm min^{-1}, and those under intense magnetic gradients were 1.2 mm min^{-1} (-1500 $T^2\,m^{-1}$) and 2.5 mm min^{-1} ($+1200\,T^2\,m^{-1}$). Thus, the speed was reduced by about 25% by applying a $-1500\,T^2\,m^{-1}$ field and was increased by about 50% by applying a $+1200\,T^2\,m^{-1}$ field.

The initial movements of the blue PI solution shown in Fig. 4 could be explained by the force, ΔF, acting on the PI solution when the convection due to its non-uniform radial temperature distribution was neglected, Eq. 1.

$$\Delta F = -(\rho_2-\rho_1)gV + (\chi_2-\chi_1)(1/\mu_0)VB\partial B/\partial z + (\chi_{PI}-\chi_{WSD})c(1/\mu_0)VB\partial B/\partial z, \quad (1)$$

where ρ_1 and ρ_2 respectively denote the densities of water in the bulk and PI solutions, g is the gravitational acceleration constant of the Earth, V is the volume of the PI solution, χ_1 and χ_2 are the respective volume magnetic susceptibilities of water in the bulk and PI solutions, μ_0 is the magnetic permeability in vacuum, B is the magnetic flux density, $\partial B/\partial z$ is the gradient of B in the vertical direction z, χ_{PI} and χ_{WSD} respectively indicate the mole magnetic susceptibilities of PI and WSD, and c is the WSD concentration. Here, the solution density was assumed to be equal to that of the solvent because the concentrations of the solutes were low. The first term of the right-hand side of Eq. 1 is the buoyancy resulting from earth's gravity, the second term is the magnetic force attributable to the magnetic susceptibility change of water, and the last term is the magnetic force attributable to the solute.

For a rough estimation, the values of ΔF in different magnetic fields were evaluated. From photon energy of the laser (2.25 mJ) and the volume of the PI solution ($\pi \times 3^2\,mm^2 \times 0.74$ mm) and the heat capacity of water,[10] the temperature increase induced by laser irradiation was estimated to be about 0.03 K. Here, it was assumed that the penetration depth of the 355 nm light was the depth at which 90% of the light was absorbed; the conversion efficiency of light to heat was unity. Then, the density and magnetic susceptibility changes in the water attributed to temperature jumps were calculated using the temperature dependence of density and the magnetic susceptibility of water.[11,12] The magnetic susceptibility change in the solute ($\chi_{PI}-\chi_{WSD}$) was calculated as -17.6×10^{-6} $m^3\,mol^{-1}$ from their atom diamagnetic susceptibilities,[12] assuming that the quantum yield of photoisomerization was unity.

All results are summarized in Table 1. In a zero field, the buoyancy induced by light absorption was about 7.6×10^{-2} $N\,m^{-3}$. Because of this force, the PI solution moved upward in a zero field. In magnetic fields, the magnetic forces due to the magnetic susceptibility change in water and that of the WSD photoisomerization were added. However, the contribution of the latter was about one order of magnitude less than that of the former; the movement of PI solution was predominantly attributed to the magnetic force acting on the heated water. At $+1200\,T^2\,m^{-1}$, the convection of water was accelerated because ΔF is about 50% larger than that at -100 $T^2\,m^{-1}$. In contrast, the convection of water was partially suppressed by applying a $-1500\,T^2\,m^{-1}$ field because ΔF is about 50% smaller than at $-100\,T^2\,m^{-1}$. The experimental results indicated that the effect of a $-1500\,T^2\,m^{-1}$ field (25%) was smaller than that of a $+1200\,T^2\,m^{-1}$ field (50%). This small difference occurs probably because of the convection caused by the non-uniform radial temperature distribution and/or the bottom surface which prevents downward motion of the PI solution.

Mogi et al.[3] have studied magnetic field effects on the thermal convection of water using a hybrid magnet. Their observations of heat transfer in water using a liquid-crystal sheet with thermochromism have shown that thermal convection of water at 308–313 K is suppressed considerably by application of a $1360\,T^2\,m^{-1}$ field when the temperature difference between bulk water and hot water is 1 K. The magnetic susceptibility and the density of water depend on temperature; according to their calculation, a 2500–3000 $T^2\,m^{-1}$ field is necessary to suppress the convection of water at 298 K when the temperature difference is 1 K. Present results concur with their calculation because the convection of water at room temperature was suppressed partially by a $-1500\,T^2\,m^{-1}$ field. As described in precedent studies,[3,12] water is a special solvent. Mass magnetic susceptibility of water is temperature-dependent, although those of most organic solvents, such as ethanol, acetone, and benzene, are temperature-independent. With increasing temperature, the absolute value of the mass susceptibility of water increases gradually. Consequently, the volume magnetic susceptibility changes that occur by temperature jumps become very small because the volume magnetic susceptibility is the product of a mass susceptibility and density. Therefore, a

large $B\partial B/\partial z$ is required to suppress the thermal convection of water.

In a previous paper,[7] we have reported the laser-induced convection of benzene in magnetic fields using a photochromic reaction of benzene-soluble diarylethene. The temperature of a thin disk of its isomer solution increases about 0.4 K by irradiation with a 308 nm laser (ca.13.5 mJ). The colored thin disk stays on the bottom surface for some time and then moves upward in one mass. The initial speed of the solution, which is about $0.4\,\mathrm{mm\,s^{-1}}$, is unaffected by magnetic fields, but the retention time of the solution on the bottom surface increases by application of a $-1300\,\mathrm{T^2\,m^{-1}}$ field and decreases by application of a $+1000\,\mathrm{T^2\,m^{-1}}$ field. The influence on the retention time has been interpreted in terms of the pressure on the PI solution, which is obtained by substituting the volume of PI solution, V, in Eq. 1 with the height of the solution. No magnetic field effect on the lift speed can be attributed to the fact that the speed is controlled by the friction force of the bulk solution because the speed is as fast as $24\,\mathrm{mm\,min^{-1}}$. Present results are analogous to those for benzene convection studied using the photochromic reaction. Whether a magnetic field affects the removal time or lift speed seems to depend on the adhesive force to a quartz cell and the viscosity of the photoisomer solution.

Magnetic field effects on benzene convection were examined further using a photo-imaging reaction of diphenylamine and carbon tetrabromide.[8] Upon UV-irradiation, a thin disk of colored solution resulting from photoproducts was generated at the bottom surface of a cell and moved upwards. The lift speed of the solution was accelerated by application of a $-1200\,\mathrm{T^2\,m^{-1}}$ field and was suppressed by application of a $+1000\,\mathrm{T^2\,m^{-1}}$ field, contrary to the results obtained using the photochromic reaction. This discrepancy was explained on the basis of the solute concentration used. In the case of the photo-imaging reaction, solute concentrations were as high as $0.02\,\mathrm{mol\,dm^{-3}}$; however, in the case of photochromic reaction, the solute concentration was $1.5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. The contribution of magnetic forces on solute to ΔF could not be neglected at high solute concentrations, as shown by the last term of the right-hand side of Eq. 1. Therefore, if the susceptibility change of solutes is opposite to that of solvent, the direction of the net magnetic force becomes opposite when solute concentrations are high.

Furthermore, in the case of the photo-imaging reaction, a shape change in the colored solution in magnetic fields was observed and was tentatively ascribed to the inhomogeneous radial magnetic field in the bore tube, generating a magnetic force in a radial direction. However, it seems that a non-uniform radial temperature distribution could be another cause for the shape change of the colored solution in magnetic fields.

As discussed above, the difference between the influence of the magnetic field on water convection and that on benzene convection is the temperature dependence of their mass susceptibility. The mass susceptibility of water is temperature-dependent, whereas that of benzene is temperature-independent. Therefore, magnetic control is difficult in water as compared to benzene. Nevertheless, it was possible to control partially the thermal convection of water as well as benzene by applying a magnetic field using a commercially available magnet.

Conclusion

Magnetic field effects on the laser-induced thermal convection of water (diamagnetic) were studied using a photochromic reaction of WSD. The lift speed of the PI solution increased by about 50% upon application of a $+1200\,\mathrm{T^2\,m^{-1}}$ field; it decreased by about 25% when a $-1500\,\mathrm{T^2\,m^{-1}}$ field was applied. The results could be explained semi-quantitatively in terms of the magnetic force acting on the PI solution. Further studies to elucidate the detailed mechanism are in progress.

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