Photo-induced convection of benzene solution of diphenylamine and carbon tetrabromide in high magnetic fields

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The influence of vertical magnetic fields on the photo-induced thermal convection of a benzene solution was studied qualitatively by using a photo-imaging reaction of DPA-CBr_4. By applying the magnetic field of -1200 T^2m^{-1}, the thermal convection of the photo-induced colored solution is enhanced, whereas it is suppressed by applying the field of +1000 T^2m^{-1}. The effect is explainable when the magnetic susceptibility of the colored solution is smaller than that of the bulk solution. The behavior of the colored solution is dependent on both the solute concentration and irradiation time. These dependencies are interpreted in terms of the photon energy absorbed by the photo-irradiated solution.

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1. Introduction

A magnetic field is a useful tool to control various chemical and physical processes [1,2]. For example, we have succeeded to control rates of organic photochemical reactions [3] and 3-dimensional morphology of inorganic membrane tubes [4,5], to align organic and inorganic crystals [6,7] and carbon nanotubes [8], and to improve crystallographic quality of protein crystals [9] by using high magnetic field. In the case of protein crystallization, the vertical magnetic fields were applied to reduce the concentration-induced convection of the protein solution by compensating for the gravitational force with the magnetic force. Another type of convection is the thermal convection which is equally an important process affecting reaction rate, yield and others. The effects of high magnetic fields on the thermal convection of liquid solution were reported [10-12]. Mogi *et al.* [11], for example, studied temperature distribution of water in magnetic fields by using a thermochromic liquid crystal sheet. In a previous paper [12], we reported the influence of magnetic fields on the transient behavior of thermal convection of a benzene solution. In that experiment, organic photochromic reaction was used for local heating the solution and visualization of convection. However, detailed mechanism of convection is still an open question.

In this paper, we have studied photochemical reaction of diphenylamine (DPA) and carbon tetrabromide (CBr_4) in benzene, in order to clarify experimental factors affecting magnetic control of thermal convection. The photoreaction of DPA and CBr_4 is well known as a photo-imaging reaction [13-15]. In this reaction, a colorless solution turns to green immediately after UV-irradiation due to the formation of a photoproduct having a visible absorption band at about 670 nm. A part of absorbed photon energy is used to heat the photochemically-generated colored solution. Therefore, this reaction is suitable for *in situ* observation of thermal convection in magnetic fields.

2. Experimental

Diphenylamine (Wako, special grade; DPA), carbon tetrabromide (Wako, special grade; CBr_4), and benzene (Nakarai Tesque, UV-spectrograde) were used as received. Benzene solution of DPA and CBr_4 was deaerated by passing through argon gas for 10 min before UV-irradiation.

In situ observation of photo-induced thermal convection was carried out using a vertical superconducting magnet (JASTEC, JMTD-LH15T40). Its room-temperature (RT) bore tube was 40 mm in diameter. Magnetic field intensity distribution in the tube was given in Fig. 1(a). The maximum magnetic field (B_{max}) and the product ($(B\partial B/\partial z)_{max}$) of the maximum field and its gradient were 15 T and 1500 T^2m^{-1}, respectively. Experimental setup for *in situ* observation was shown in Fig. 1(b). A 10 mm × 10 mm × 40 mm quartz cell containing a benzene solution of DPA -CBr_4 was placed in a bore tube of a superconducting magnet. The solution was irradiated from its bottom through a 6-mm hole by a UV-light from a super-high pressure xenon lamp (Ushio, UXL-500-O) with a UV band-path filter (Sigma Koki, UTVAF-34U; 280-380 nm) and a 5-cm water filter. The experiments were carried out at room temperature. Magnetic fields were varied by placing the cells at the different positions in the bore tube. The movement of the colored solution after photo-irradiation was observed by a combination of a CCD camera and a video recorder and was analyzed by a software (Library, Move-tr32).

3. Results

Influence of Solute Concentration: Upon UV-irradiation of a benzene solution of DPA-CBr_4, a colored photoproduct is formed,

$$\text{DPA} + CBr_4 + h\nu \rightarrow \rightarrow \rightarrow \text{Photoproduct (abs. max. = ca. 670 nm)}$$

A photoproduct which has an absorption band maximum at ca. 670 nm was reported to be diphenylamine cation radical or diphenylamino radical [14,15]. However, this assignment does not seem to be confirmed, as the photochemical reaction of DPA and CBr_4 is highly complex. Therefore, hereafter we simply call it as a photoproduct.

Figure 2 shows sequential photos of a 0.025 M benzene solution of DPA-CBr_4 after UV-irradiation in magnetic fields. Upon the UV-irradiation, a disk-like thin layer of the solution at the bottom surface of the vessel changes its color to green due to the formation of a colored photoproduct, and the upper surface of the colored solution, heated by photon energy, moves totally upwards, thought photos in Fig.2 are dim and pale. At 10 T (-1200 T^2m^{-1}) the upper surface of the colored solution moves upwards from the radial center of the layer faster than that at zero field (0T (0 T^2m^{-1})). In order to show the movement of the colored solution clearly, the vertical positions of the front of the colored solution were analyzed from the video pictures. Figure 3 shows the movement of the front of the colored solution in magnetic fields. The behavior of the solution is different in different magnetic fields. The time dependence of the behavior of the solution is divided into two parts. Firstly, the solution stays on the bottom surface of the vessel for some time and secondly the front of the solution moves upwards. At zero field, for example, it moves upwards at a delay time of ca. 10 s after UV-irradiation start. At 10 T (-1200 T^2m^{-1}) the front of the solution moves upwards from the bottom surface faster than that at zero field. Therefore, the behavior of the solution in magnetic fields is characterized by using the retention time, *i.e.*, the time of the solution staying on the bottom surface, and the lift speed, *i.e.*, the speed of the front of the solution moving upwards in the bulk solution which is calculated from the slope of the curve shown in Fig. 3. Table 1 shows the concentration dependence of the retention time and the lift speed of the colored solution in magnetic fields. At zero field, the colored solution at low solute concentrations (0.006 and 0.0125 M) does not move from the bottom surface of the vessel. Part of the solution at higher solute concentrations (0.025 and 0.05 M) moves upwards from the upper surface, the retention time becomes shorter and the lift speed increases. The behavior of the solution at 14 T (-46 T^2m^{-1}) is similar to that at zero field. In good contrast to the solution behavior at zero field, part of the solution at 10 T (-1200 T^2m^{-1}) always moves upwards and with increasing the solute concentration, the retention time decreases and the lift speed increases. At 10 T (+1000 T^2m^{-1}), part of the solution moves upwards when the solute concentration becomes higher (0.05 M). The facts that the solution behavior at 14 T (-46 T^2m^{-1}) is similar to that at zero field (0 T, 0 T^2m^{-1}) and that the behavior at 10 T (-1200 T^2m^{-1}) is different from that at 10 T (+1000 T^2m^{-1}) indicate that not a magnetic flux density, B, but the product, $B\partial B/\partial z$, of the density and its gradient is responsible for the behavior of the solution in magnetic fields. From the above results, it is concluded that thermal convection of a benzene solution can be controlled by applying vertical magnetic fields and that there is an optimum concentration suitable for controlling the thermal convection. At a solute concentration of 0.025 M, the thermal convection rate can be enhanced six times by application of -1200 T^2m^{-1} or can be completely suppressed by application of +1000 T^2m^{-1}.

Influence of Irradiation Time: The influence of irradiation time was also examined for the 0.025 M solution. Table 2 shows the influence of irradiation time on the behavior. Some interesting features of the influence will be derived from the table, though its experimental conditions, *i.e.*, light intensity and magnetic flux density, are slightly different from those shown in Table 1. At zero field, the colored solution does not move from the bottom surface at a UV-irradiation time of 4 s, while part of the solution moves upwards at a time of $\geq$ 10 s. In magnetic fields, the behavior of the solution is different depending on the direction of magnetic force. At -1400 T^2m^{-1}, the retention time and the lift speed do not change significantly with increasing the irradiation time. The UV-irradiation, after starting the upward movement of the colored solution, does not affect significantly the convection of the colored solution. At +1200 T^2m^{-1}, the solution does not move under a short irradiation time (4-20 s) and, after the prolonged irradiation (30 s), part of the solution moves upwards. The behavior of the solution at -57 T^2m^{-1} (14T) is similar to that at zero field. From the above-mentioned observations, it is concluded that there is an optimum irradiation time suitable for controlling the thermal convection of the benzene solution. In the present case, the irradiation time between 4 and 10 s may be suitable for controlling the convection. Small differences in the values at 4 s irradiation between in Tables 1 and 2 are due to the facts that the UV-light intensity and magnetic flux density are slightly different in two experiments.

4. Discussion

Upon UV-irradiation, the photon energy absorbed by the benzene solution of DPA-CBr_4 is used partly to induce photochemical reaction of solutes, forming a colored photoproduct and partly to heat the colored photoproduct solution. The force, ΔF, acting on the colored solution in magnetic fields are given by equation (1),

$$\Delta F = (\rho_A - \rho_B)gV \quad + (1/\mu_0)(\chi_B - \chi_A)VB\partial B/\partial z \qquad (1)$$

where, ρ_A and ρ_B are the densities of the bulk DPA-CBr_4 solution (A) and the colored solution (B), respectively, χ_A and χ_B are the magnetic susceptibilities of the solution A and the solution B, respectively, V is the volume of the colored solution, g is the earth gravity, μ_0 is the magnetic permeability of vacuum, B is the magnetic flux density and $\partial B/\partial z$ is the gradient of B in the vertical direction, z. The first term of the right-hand side of equation (1) is the gravitational force due to the density changes of the solution induced by photo-irradiation, consisting of the volume change of benzene due to temperature jump and that of the solutes due to photoreaction. The second term is the magnetic force due to the magnetic susceptibility difference, consisting of the volume change of benzene due to temperature jump and that of the solutes induced by photoreaction. When ΔF becomes larger than the surface tension of the colored solution to the bottom surface of the vessel, the solution moves upwards from the bottom surface. The lift speed of the solution in the bulk solution is determined by the balance of ΔF and the friction force of the bulk solution to the colored solution.

At zero field, the behavior of the heated colored solution is determined by the first term of the right-hand side of equation (1). Part of the solution moves upwards because its density is smaller than that of the bulk solution. In the presence of magnetic fields, magnetic forces affect the movement of the solution, since magnetic susceptibility of the colored solution is different from that of the bulk solution. Therefore, the interesting results shown in Section 3 can be explained in terms of the magnetic forces acting on the bulk and colored solutions. The magnetic field effects on the retention time are related to the force ΔF and the surface tension of the colored solution to the vessel surface, whereas those on the lift speed are related to the balance of ΔF and the friction force of the bulk solution acting on the colored solution. There is a strong relationship between the effects of magnetic force on retention time and those on lift speed.

The influence of the solute concentration shown in Table 1 can be explained by the influence of the volume change of the photo-generated colored solution. The thickness of the photo-generated colored solution decreases by 8 times with increasing the solute concentration from 0.006 M to 0.05 M, as the absorbance of the DPA-CBr_4 solution changes at least 8 times. Therefore, at a constant irradiation time, the temperature and therefore density change of the colored solution increases by 8 times with increasing the solute concentrations. At 0 T (0 T^2m^{-1}), the movement of the colored solution is governed by the first term of the right-hand side of equation (1). Whether part of the colored solution moves upwards or not is determined by the density change caused by UV-irradiation. Only when ΔF due to the density decrease in the colored solution is sufficiently large, part of the colored solution can move upwards from the bottom surface. In the presence of magnetic fields, the sum of buoyancy and magnetic force determines the movement of the solution. The observations that part of the colored solution at -1200 T^2m^{-1} moves upwards at a retention time shorter than that at zero field, whereas part of the solution at + 1000 T^2m^{-1} does at a retention time larger than that at zero field, can be explained only when $\chi_B < \chi_A < 0$. Under this condition, the magnetic force at -1200 T^2m^{-1} is upward, accelerating the upward movement of the colored solution, whereas the force at +1000 T^2m^{-1} is downwards, suppressing that of the solution. With increasing temperature, the density of benzene decreases and, as a result, the volume magnetic susceptibility of benzene increases. Thus the observed effects may be explainable by taking into account of the magnetic susceptibility of solutes in addition to that of solvent (benzene), though the molar ratios of the solvent to solutes are roughly estimated to be smaller than 100: 1 in the present experimental condition. It is interesting that small magnetic susceptibility change of the solutes affects remarkably the behavior of the solution significantly in magnetic fields.

The effects of magnetic fields on the lift speed are explained similarly. However, the effects are not always parallel to those on the retention time. It is because the lift speed of the colored solution is determined mainly by the balance of ΔF and the friction force of the bulk solution to the colored solution, whereas the retention time is determined by the balance of ΔF and the surface tension. At large ΔF the lift speed reaches to a steady state value.

Influence of irradiation time shown in Table 2 is similarly explained by the influence of temperature of the colored solution. By increasing the irradiation time, the photon energy absorbed increases and the temperature of the colored solution increases, as the solute concentration is constant. At a short irradiation time of 4 s, ΔF is not strong enough to move part of the solution from bottom surface at zero field. By applying the upward magnetic force, part of the solution moves upwards. At the irradiation time of 10 s the convection of the solution is controlled by the application of magnetic fields. By prolonged irradiation of 30 s, the solution becomes so hot that part of the solution moves upwards regardless of magnetic fields, the speed being controlled by the friction force of the bulk solution to the colored solution.

Temperature change induced by UV-irradiation is not evaluated in this experiment, since the UV-light is polychromatic, and, therefore, density and magnetic susceptibility changes induced by UV-irradiation are not estimated. However, it is speculated that a density change of 0.6 kg m^{-3} or so and a magnetic susceptibility change of 5×10^{-3} $JT^{-2}m^{-3}$ or so might induce the convection of the solution in magnetic fields, on the analogy of the previous work [12].

So far we have discussed the vertical movement of the colored solution in magnetic fields. However, the magnetic field also affects the shape of the floating colored solution, as schematically shown in Fig. 4. At zero field, upper surface of the colored solution moves upwards entirely. In a magnetic field of -1200 T^2m^{-1}, the solution moves upwards from the radial center of the layer. This shape change may be partly attributable to the influence of the magnetic force in the radial direction (r) in the bore tube. The product ($B\partial B/\partial r$) of the magnetic flux density and its gradient in the radial direction (r) in the tube is about +50 - +100 T^2m^{-1} at $r = 5$ mm at the locations where effects of vertical fields are examined. Therefore, because of this radial magnetic force, the colored solution may shrink to the radial center of the layer in magnetic fields during the movement.

Finally the magnetic field effect on the relative yield of colored compound was preliminarily examined. The relative yield of the colored product was obtained from its absorbance at 650 nm. The yield decreases by about 12% by application of 2.9 T (+97 T^2m^{-1}) and decreases very slightly (3 %) by application of 2.6 T (-102 T^2m^{-1}), whereas the magnetic field of 4 T (4 T^2m^{-1}) does not affect the yield. The results suggest that not the magnetic flux density but the product of magnetic flux density and its gradient affects chemical yields, indicating the thermal convection affects slightly the yield of photoproduct, if any.

In a previous paper [12], we examined the photo-induced thermal convection of benzene solution of a photochromic compound, 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethane. The retention time of the photo-generated photoisomer solution is 5 s at zero field. It increases to 9 s by application of $-1300\ \mathrm{T^2m^{-1}}$, whereas it decreases to 3 s by application of $+1000\ \mathrm{T^2m^{-1}}$. These observations are opposite to the above-mentioned results. This fact also indicates that small change in the magnetic susceptibility of solutes seems to contribute remarkably the behavior of the thermal convection of benzene solution in magnetic fields.

Evans *et al*. [16] studied the effects of magnetic field on the traveling wave formed during the reaction of (ethylenenediaminetetraacetato)cobalt(II) and hydrogen peroxide by magnetic resonance imaging at 7 T. The wave propagation is affected by a magnetic field gradient of $\mp 0.2\ \mathrm{T\ m^{-1}}$. The magnetic force due to the difference of magnetic susceptibility at the wave front results in the acceleration or deceleration of the wave velocities. The phenomena observed in this study are similar to those mentioned above.

4. Conclusion

The influence of vertical magnetic fields on the photo-induced thermal convection of a benzene solution was studied qualitatively by using a photo-imaging reaction of DPA-$\mathrm{CBr_4}$. The photo-imaging reaction is very useful to observe thermal convection of solution. By applying the magnetic field of $-1200\ \mathrm{T^2m^{-1}}$, the thermal convection of the photo-induced colored solution is enhanced, whereas it is suppressed by applying the field of $+1000\ \mathrm{T^2m^{-1}}$. The effect is explainable when the magnetic susceptibility of the colored solution is smaller than that of the bulk solution. The behavior of the colored solution is dependent on both the solute concentration and irradiation time. These dependencies are interpreted in terms of the photon energy absorbed by the colored solution. The temperature difference between the bulk solution and the colored solution results in changes of the retention time and lift speed of the colored solution in magnetic fields. It is suggested that small magnetic susceptibility difference of solutes between the bulk solution and the photo-irradiated solution seems to affect the behavior of the latter solution.

In this study, the influence of magnetic forces on the photo-induced thermal convection of benzene solution is discussed qualitatively. Semi-quantitative analysis of the convection of the above solution using a monochromatic UV-light is now in progress.

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Table 1 Influence of solute concentration on the retention time and lift speed of colored solution at a UV-light irradiation time of 4 s.

		Retention time, s (Lift speed, mm s^{-1})			
Concentration*	B (T)	10	14	10	0
(M)	$B\partial B/\partial z$ (T^{2}m^{-1})	-1200	-46	+1000	0
0.006		9.0 (0.8)	--- (--)	∞ (0)	∞ (0)
0.013		6.0 (1.7)	12 (0.3)	∞ (0)	∞ (0)
0.025		5.0 (2.5)	6.5 (0.3)	∞ (0)	10 .0 (0.4)
0.050		1.5 (2.2)	1.5 (2.8)	1.5 (3.6)	1.5 (2.7)

*Concentrations of DPA and CBr_4 are the same.

Table 2 Influence of the UV-irradiation time on the retention time and lift speed of colored solution for the 0.025 M solution.

		Retention time, s (Lift speed, mm s^{-1})			
Irradiation	B (T)	10	14	10	0
Time, s	$B\partial B/\partial z$ (T^{2}m^{-1})	-1400	-57	+1200	0
4		6.8 (3.5)	15.9 (0.3)	∞ (0)	∞ (0)
10		5.5 (3.5)	8.6 (3.2)	∞ (0)	9.3(3.5)
20		6.6 (4.0)	9.3 (4.0)	∞ (0)	9.3(2.7)
30		5.5 (4.0)	9.1 (5.9)	13.2 (1.2)	9.1(2.9)

Figure Captions

Fig. 1. (a) Vertical distribution of magnetic flux density (*B*) and the product ($B\partial B/\partial z$) of the density and its gradient along the magnet bore tube axis. (b) Experimental setup for *in situ* observation of photo-induced thermal convection in a magnet bore tube.

Fig. 2. Sequential photos of the photo-induced thermal convection of benzene solution in magnetic fields (side view). The colored solution moving upwards at 0 T (0 T^2m^{-1}) and 14 T (-46 T^2m^{-1}) is indicated by arrows, since its color is dim and pale. White portion in the photos are due to the scattering light from background. Concentrations of DPA and CBr_4 are 0.025 M and UV-irradiation time is 4 second.

Fig. 3. Time dependence of the front position of the colored solution in magnetic fields. Concentrations of DPA and CBr_4 are 0.025 M and UV-irradiation time is 4 second.

Fig. 4. Schematic representation of the movement of the front of the colored solution in (a) the absence and (b) the presence of magnetic field of -1200 T^2m^{-1}. Arrows indicate the movement of the front of the colored solution.

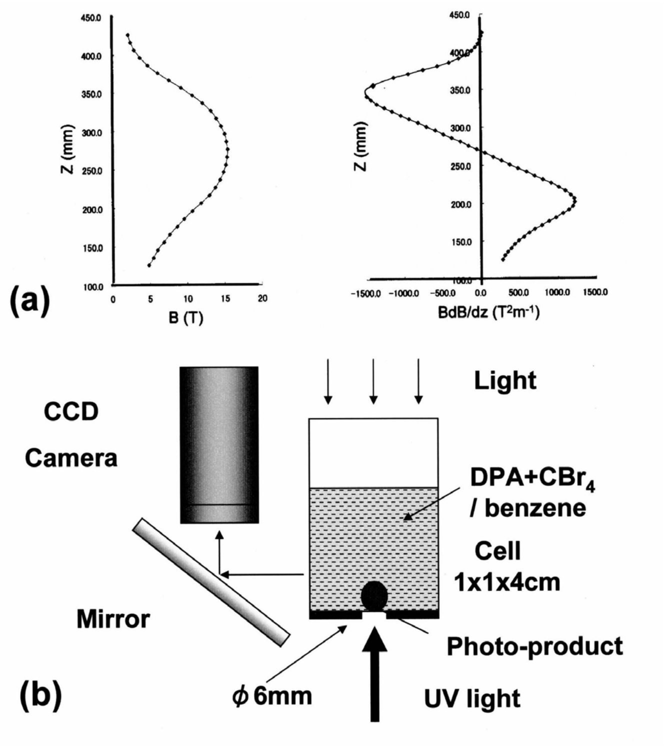

450.0
400.0
350.0
300.0
250.0
200.0
150.0
100.0
Z (mm)
0
5
10
15
20
B (T)
(a)
-1500.0
-1000.0
-500.0
0.0
500.0
1000.0
1500.0
BdB/dz (T²m⁻¹)
CCD
Camera
Light
DPA+CBr4
/ benzene
Cell
1x1x4cm
Mirror
Photo-product
(b)
ϕ 6mm
UV light

Figure 1

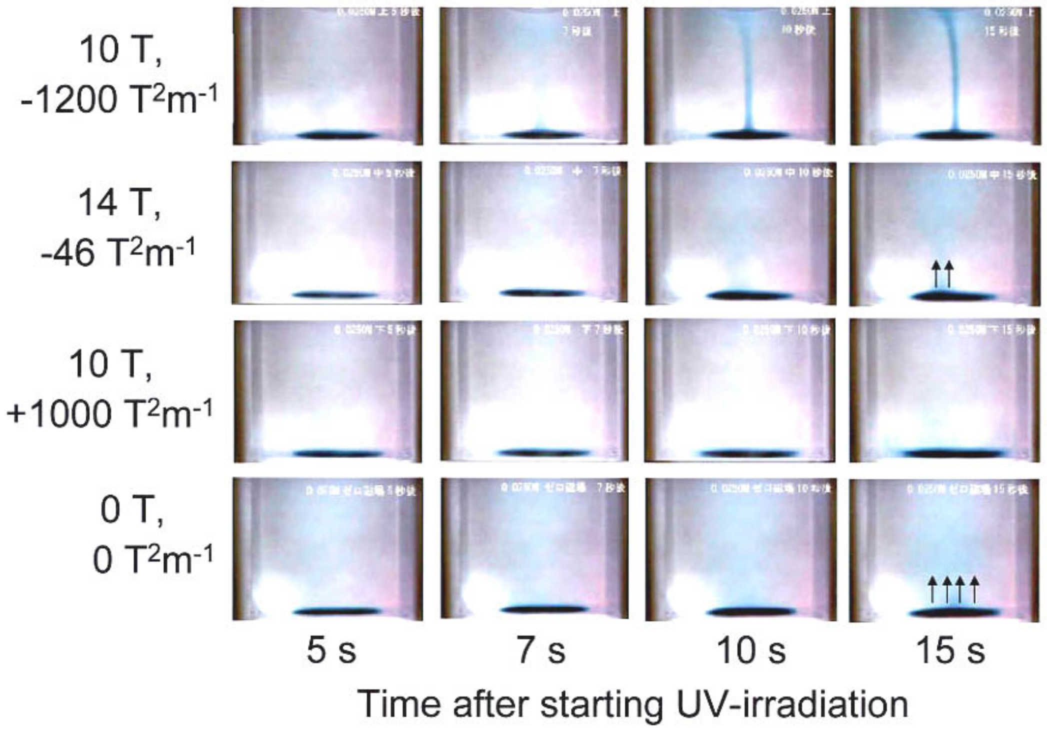
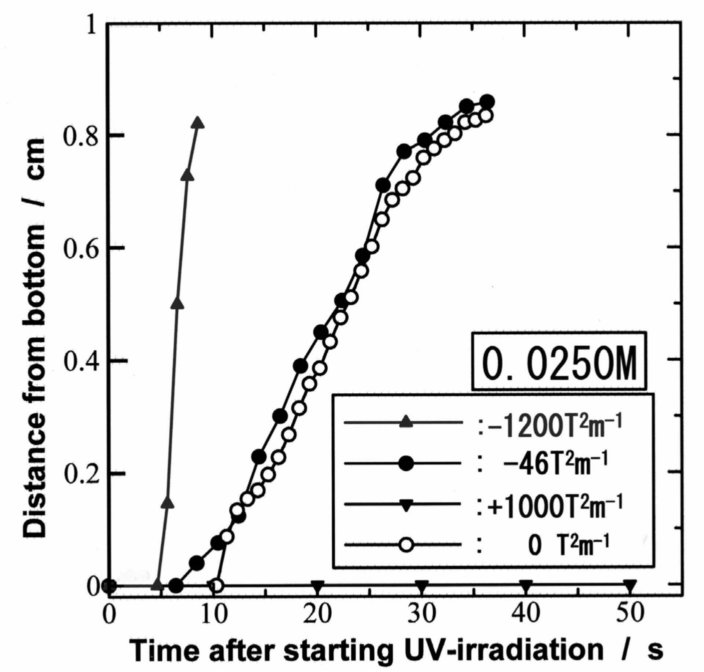

10 T, -1200 T²m⁻¹
14 T, -46 T²m⁻¹
10 T, +1000 T²m⁻¹
0 T, 0 T²m⁻¹
5 s
7 s
10 s
15 s
Time after starting UV-irradiation

Figure 2



1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
Distance from bottom / cm
Time after starting UV-irradiation / s
0.0250M
:−1200T²m⁻¹
: −46T²m⁻¹
:+1000T²m⁻¹
: 0 T²m⁻¹

Figure 3

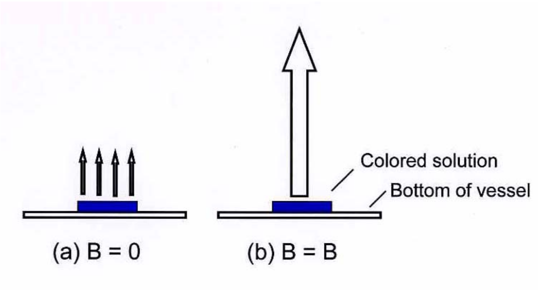


Figure 4