1. Introduction – What is Magneto-Science? –

All substances consist of atoms. All atoms comprise electrons and nuclei. Because the spin and orbital motions of electrons produce magnetism, no substance is without magnetism. Therefore, it is reasonable to expect that chemical and physical behaviors of all substances are affected to some degree by a magnetic field. Magneto-science deals with the influence of magnetic fields on chemical, physical, and biological phenomena and the application of magnetic fields in industry.

The effects of static magnetic fields on chemical and physical processes have been discussed elsewhere in detail [1]. Those effects are divisible into three groups, as shown in Table 1. The first, quantum mechanical effects, arise from the interaction of electron spins in short-lived reaction intermediates called radical pairs. In photochemical reactions of organic molecules, radical pairs are generated as intermediates. Product yields and radical pair lifetimes are affected by an external magnetic field (MF). The second is thermodynamic effects. Crystals are often oriented in one direction when crystallization occurs in an MF. This orientation happens when a crystal is magnetically anisotropic. The third is mechanical effects, consist of three mechanisms. In electrochemical reactions, the transport of reactants in bulk solution to electrodes is a key process. The motion of ions and electrons in the solution is affected by Lorentz force. The magnetic force is well-known to be proportional to the product of magnetic flux density and its gradient. One application is magnetic levitation of diamagnetic materials. Magnetic susceptibility force, which is proportional to the product of the magnetic susceptibility gradient of solutes in solution and the square of magnetic flux density, is operative in crystal growth from solution. Examples of these effects will be presented.

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Type of effect	Type of MF	Mechanism	Example
Quantum	Homogeneous	Radical pair	Photochemical
mechanical effect		mechanism	reaction
Thermodynamic	Homogeneous	Anisotropic magnetic	Magnetic
effect		energy	orientation
Mechanical effect	Homogeneous	Lorentz force	Electrochemical
			reaction
Mechanical effect	Inhomogeneous	Magnetic force	Magnetic
			levitation
			Magnetically
			simulated
			microgravity
Mechanical effect	Homogeneous	Magnetic	Crystal growth
		susceptibility force	

Table 1 Classification of magnetic field effects

1. Quantum Mechanical Effect – Radical Pair Mechanism

In chemical reactions such as decomposition, electron transfer, and hydrogen transfer, a pair of radicals is often generated as a short-lived reaction intermediate in a solvent cage. It is designated as a radical pair (RP). Reaction pathways of RP generated by decomposition of a molecule, A–B, are given in Fig. 1. This pair has two electron spin states, singlet (S) and triplet (T), in which T comprises three sublevels: T_+ , T_0 , and T.. Magnetic interaction in a pair induces spin transitions where energies of the S and T



B = B



B = 0

states are nearly degenerate. At a zero field, S, T_+ , T_0 , T. are energetically degenerate. Spin transitions among all spin states take place because of electron–nuclear hyperfine interaction (hfi) (Fig. 2). When a magnetic field is applied, T_+ and T. mutually separate because of the electronic Zeeman interaction. Consequently, the rates of S-T₊ and S-T. transitions are reduced in a magnetic field. Therefore, the cage product and escape product yields are affected by an MF. To obtain a large magnetic field effect, a radical pair must have a sufficiently long lifetime so that hfi-induced spin transitions occur at a zero field. Micellar solutions are often used because a micelle provides an ideal cage for an organic radical pair

dissolved in it.

Magnetic field effect (MFE) onphotosensitized oxidation of1,3-diphenylisobenzofuran(DPBF) in sodium dodecyl sulfate(SDS) micellar solution[2,3].Figure 3 portrays UV spectralchanges of an aerated SDSmicellar solution of anthraquinone



Fig. 3. UV Spectral change of aerated SDS solution of AQ and DPBF.

(AQ) and DPBF. Upon photo-irradiation of AQ, DPBF is oxidized to dibenzoylbenzene (DBB). In a zero field, intensities of the absorption bands of AQ (320 nm) and DPBF (410 nm) decrease gradually with irradiation time. In a 0.1 T field, the DPBF degradation is enhanced significantly. The MFE on the degradation yields of AQ and DPBF and the formation yield of DBB was examined using high performance liquid chromatography (HPLC). The results are presented in Fig. 4. The degradation yield of AQ was reduced by 10% at 0.2 T, whereas the

degradation yield of DPBF and the formation yield of DBB increased by 50–60% at 0.2 T.

Details of MFE on photochemical reaction of AQ in a de-aerated SDS micellar solution have been elucidated. The reaction mechanism of AQ is the following.



Fig. 4. MFE on the yield of DPBF, AQ and DBB.

$$AQ + hv \rightarrow {}^{1}AQ^{*} \rightarrow {}^{3}AQ^{*}$$
(1)
$${}^{3}AQ^{*} + HS \rightarrow {}^{3}(AQH \cdot S)$$
(2)

$$^{3}(AQH \cdot S) \rightarrow ^{1}(AQH \cdot S)$$
 (3)

$$^{3}(AOH \cdot \cdot S) \rightarrow AOH \cdot + \cdot S \rightarrow$$

$$\rightarrow$$
 AQH-AQH, AQH-S, S-S, AQ (4)

$$^{3}(AQH \cdot \cdot S) \rightarrow AQH \cdot S$$
 (5)

Upon photo-irradiation, the excited triplet AQ, ${}^{3}AQ^{*}$, is generated. It undergoes hydrogen abstraction from dodecyl sulfate (HS), generating a triplet radical pair, ${}^{3}(AQH \cdot \cdot S)$, comprising an anthrasemiquinone radical (AQH \cdot) and a dodecyl sulfate radical ($\cdot S$). At a zero field, the triplet pair undergoes spin transitions to singlet radical pair ${}^{1}(AQH \cdot \cdot S)$ as well as dissociation of the pair, yielding escape products AQH-AQH, AQH-S, S-S, and AQ. By application of a magnetic field, the yields of escape products increase because of the suppression of T \rightarrow S spin transitions.

Degradation of DPBF occurs only in aerated solution containing AQ. Based on these findings we propose the following reaction mechanism.

$AQH^{\cdot} + O_2 \rightarrow AQHO_2^{\cdot} \rightarrow AQ + HOO^{\cdot}$	(6)
$HOO + DPBF \rightarrow DBB$	(7)

The degradation yield of DPBF and therefore the formation yield of DBB increases as the yield of oxidation initiator increases by application of MF.

2. Thermodynamic Effect – Anisotropic Magnetic Energy – Magnetic Orientation –

Magnetic energy, *E*, of a molecule is given as follows.

$$\boldsymbol{E} = (1/2\mu_0)\boldsymbol{\chi}\boldsymbol{B}^2$$

(8)

Therein, $\boldsymbol{\chi}$ is the magnetic susceptibility of the molecule. Usually a molecule has anisotropic magnetic susceptibilities. Therefore, the magnetic energy is orientation-dependent and the molecule undergoes molecular orientation to the most stable direction. However, the magnetic energy of a molecule is extremely small compared to the thermal temperature. energy at room Consequently, no orientation of a single molecule is achieved at room temperature. In contrast, aggregates that have an ordered structure such as crystal can obtain anisotropic magnetic energies greater than the thermal energy at room



Fig. 5. Magnetic orientation of carbon nanotubes.

temperature because the anisotropic energy of an aggregate increases concomitantly with increasing volume, whereas its translational thermal energy, randomizing its orientation, is constant, irrespective of volume.

<u>Magnetic orientation of carbon nanotubes</u> [6]. Figure 5 depicts carbon nanotubes prepared from their solution suspension using solvent evaporation. At a zero field, carbon nanotubes (white lines in the figure) are oriented randomly. In an 8 T field, they are oriented in parallel to the field. The magnetic orientation of carbon nanotubes is achieved even though they are as short as a few micrometers.

3. Mechanical Effect – Lorentz Force

When a particle with an electric charge e moves at a velocity v in a magnetic field **B**, it receives Lorentz force $F_{\rm L}$ (Fig. 6),

(9)

$$\boldsymbol{F}_{\mathrm{L}} = (1/\mu_0) \boldsymbol{e} \boldsymbol{v} \times \boldsymbol{B}$$

where μ_0 is the magnetic permeability of vacuum. In electrochemical reaction solutes in bulk solution must move to electrodes as the reaction takes place at electrodes. Therefore many examples of MFE based on Lorentz force have been reported. As described in



this paper, the MFE on non-electrochemical reaction will be presented.

<u>MFE on silicate garden (chemical garden) reaction</u> [4,5]. The silicate garden reaction is a famous reaction that is used popularly for chemical demonstrations. The reaction is simple. When metal salt crystals are put into an aqueous solution of sodium silicate, they grow upward in the solution in semi-permeable tubes within an hour or so.

 $Na_2Si_2O_5 + ZnSO_4 \rightarrow Zn(OH)_2\downarrow + SiO_2\downarrow$ (10)

Figure 7 depicts the influence of strong vertical magnetic fields on the tube morphology when zinc sulfate crystals are used. At a zero field, membrane tubes grow upward. In the presence of a 6 T vertical field, it grows helically in a



Fig. 7. MFE on silicate garden reaction.

right-handed direction. When the field direction is reversed, the tube grows helically with a left-handed direction. The chirality of the tube is controlled magnetically.

A concentrated solution of metal salt flows out from the top of the tube. The motion of ions in the solution is affected by the Lorentz force. The direction of the helix is determined by the relative relation between the tube and the vessel wall.

4. Mechanical Effect – Magnetic Force and Magnetic Susceptibility Force

Two forces are derived from magnetic energy (eq. 8) when two parameters X and B are distance (*z*)-dependent.

$$\boldsymbol{F} = -\partial \boldsymbol{E}/\partial \boldsymbol{z} = (1/\mu_0) \boldsymbol{\chi} \boldsymbol{B} \partial \boldsymbol{B}/\partial \boldsymbol{z} + (1/2\mu_0) (\partial \boldsymbol{\chi}/\partial \boldsymbol{z}) \boldsymbol{B}^2$$
(11)

The first term of the right-hand equation is designated as the magnetic force (F_{mag}). The second term is tentatively called the magnetic susceptibility force (F_{sus}).

$$\boldsymbol{F}_{\text{mag}} = (1/\mu_0) \boldsymbol{\chi} \boldsymbol{B} \partial \boldsymbol{B} / \partial \boldsymbol{z}$$
(12)

$$\boldsymbol{F}_{\rm sus} = (1/2\mu_0)(\partial \boldsymbol{\chi}/\partial z)\boldsymbol{B}^2 \tag{13}$$

Actually, F_{mag} is operative only in a gradient magnetic field, whereas F_{sus} is operative when χ is inhomogeneous.

a. Magnetic Force, Magnetic Levitation, and Magnetically Simulated Microgravity

<u>Magnetic force</u>

Many examples of this effect exist. Here, the simplest example is introduced.

<u>MFE on silver crystal growth</u> [7]. When copper metal is immersed in a silver nitrate aqueous solution, metallic silver crystals deposit from the solution because of their ionization tendency.

$$2Ag^{+} + Cu \rightarrow 2Ag \downarrow + Cu^{2+}$$
(14)



a. 0 T b. 0.1 T Fig. 8. MFE on silver crystal growth.

Figure 8 portrays the MFE on the shape of silver crystal in a petri dish (diameter50 mm). In a zero field, large silver crystals grow freely around a circular copper metal (ϕ 18 mm). When the reaction is undertaken on a 0.1 T circular permanent magnet (ϕ 30 mm), the crystal growth is limited within the region where the magnetic field is active. Magnetic force prevents the solution containing paramagnetic Cu²⁺ ion from removal from the MF-active region.

<u>Magnetic levitation</u> An apple falls downward because of gravity. If an upward magnetic force equals to the gravitational force is applied, then the apple is levitated (Fig. 9).

$$mg = (1/\mu_0) \chi B \partial B / \partial z \tag{15}$$

Therein, *m* denotes the mass of an apple, *g* stands for Earth's gravity, and *x* is the diamagnetic susceptibility of the apple. The value of $B\partial B/\partial z$ necessary for water levitation is estimated roughly as 1400 T²m⁻¹.

Figure 10 shows a magnetically levitated water droplet containing a sludgeworm, as viewed from the side [8]. We can levitate many diamagnetic substances such as water, frogs, cherry tomatoes, and plastic chips.



Fig. 9. Magnetic levitation.



Fig. 10. Magnetic levitation of sludgeworm (side view).

<u>Magnetically Simulated Microgravity</u> We can generate magnetically simulated microgravity on the earth using MF because the effective gravitational force becomes zero under the conditions given in eq. 15.

For example, we were the first to report preparation of *lysozyme* crystals having X-ray-crystallographically improved quality using a superconducting magnet [9]. It is worth remembering that magnetically simulated microgravity is an environment that is analogous to a space environment, but not the same because there might exist MFEs of several types. Such environments are anticipated for preparation of new functional materials using magnetically simulated microgravity.

b. Magnetic Susceptibility Force

The effect of a horizontal magnetic field (8 T) on the growth rate of glycine crystal from aqueous solution was examined [10]. The rate decreases by about 20% by application of the homogeneous magnetic field. Glycine is amino acid, having no

net charge. Therefore, neither Lorentz force nor magnetic force can affect the growth rate. When approaching conditions in which the crystal concentration of glycine becomes non-uniform, some glycine in the solution is deposited as crystals on the crystal surface. It is proposed that the growth rate of glycine crystal is reduced by the magnetic susceptibility force, which prevents the convection necessary for solute transportation from the bulk solution to the crystal surface.

5. Biological Effects of MF

Finally, MFE on the behavior of a microorganism, *Euglena gracilis* is discussed [11]. In the absence of a magnetic field, living *Euglena* in water disperse uniformly in a petri dish (Fig. 11). When an 8 T horizontal magnetic field is applied, living *Euglena* move to a higher field after a few hours of exposure, although dead ones move to a lower field. This observation is explainable by the magnetic orientation of



Euglena.

Fig. 11. MFE on Euglena.

6. Summary

As described briefly herein, MF presents great possibilities for affecting various chemical, physical, and biological phenomena. Furthermore, several interesting effects of MF, the mechanisms of which are not explainable using the mechanisms shown in Table 1, have been reported. New MFEs will be discovered in the near future.

Magneto-science will become a key basic science supporting materials sciences, nano- and life-sciences, etc. in the twenty-first century because it presents the promise of many far-reaching technological applications to various areas of industry.

References

[1] M. Yamaguchi and Y. Tanimoto (Eds.), *Magneto-Science*, Kodansha/Springer, Tokyo, 2006.

[2] Y. Tanimoto, K. Shimizu, and M. Itoh, J. Am. Chem. Soc., 106, 7257 (1984).

[3] C. Udagawa, T. Izutani, S. Yamamoto, S. Morimoto, S. Fukuyoshi, R. Nakagaki, and Y. Tanimoto, *J. Photochem. Photobiol. A: Chem.*, **238**, 16 (2012).

[4] I. Uechi, A. Katsuki, L. Dunin-Barkovskiy, and Y. Tanimoto, J. Phys. Chem. B, **108**, 2527 (2004).

[5] W. Duan, S. Kitamura, I. Uechi, A. Katsuki, and Y. Tanimoto, *J. Phys. Chem. B*, **109**, 13445 (2005).

[6] M. Fujiwara, E. Oki, M. Hamada, Y. Tanimoto, I. Mukouda and Y. Shimomura, *J. Phys. Chem. A*, **105**, 4383 (2001).

[7] Y. Tanimoto, C. Udagawa, A. Katsuki, S. Maki, and S. Morimoto, *Bull. Chem. Soc. Jpn.*, doi:10.1246/bcsj.20130168

[8] <u>http://www.magneto-science.jp/english/gallery_en.html</u>

[9] D. C. Yin, N. I. Wakayama, K. Harata, M. Fujiwara, T. Kiyoshi, H. Wada, N. Niimura, S. Arai, W. D. Huang, and Y. Tanimoto, *J. Cryst. Growth*, **270**, 180 (2004).

[10] M. Sueda, A. Katsuki, Y. Fujiwara, and Y. Tanimoto, *Sci. Tech. Adv. Mat.*, **7**, 380 (2006).

[11] Y. Tanimoto, S. Izumi, Y. Fujiwara, M. Fujiwara, T, Hirata, and S. Yamada, *Int. J. Electromag. Mechanics*, **14**, 311 (2001/2002).