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# Control of chemical reaction involving dissolved oxygen using magnetic field gradient

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### Abstract

This study investigated the control of dissolved oxygen concentration using magnetic forces from gradient magnetic fields near a Nd–Fe–B permanent magnet. Maximum values of magnetic flux density and the product of the magnetic flux density and its gradient were 0.63 T and  $44 \text{ T}^2/\text{m}$ , respectively. The magnet was placed under a Petri dish filled with 15 ml of 10% ammonia water. The Petri dish had a copper sheet in the center. Absorbance of tetraamminecopper(II) complex produced by the reaction in oxygen was measured using a spectrophotometer to observe oxygen concentration. Results showed that the magnetic field quantitatively enhanced tetraamminecopper(II) complex production occurred in the magnetic field at less than 2 mm depth. The calculated magnetic force increase near the magnet surface supports this result. These results show that greater enhancement of the reaction rate occurs when the stronger magnetic force acts on oxygen molecules. © 2006 Elsevier B.V. All rights reserved.

Keywords: Magnetic field; Gradient; Paramagnetism; Oxygen; Copper complex

## 1. Introduction

A strong inhomogeneous magnetic field exerts a magnetic force on paramagnetic substances. Experimental studies demonstrated that convection of paramagnetic liquids [1] and gases [2–4] were controlled by strong inhomogeneous static magnetic fields. Theoretical studies provided the explanation of magnetically controlled convection of paramagnetic fluids [5,6]. Oxygen gas is a paramagnetic substance. Consequently, the movement of oxygen gas can be influenced by strong gradient magnetic fields [2]. The diffusion of dissolved oxygen molecules in water [7– 10] and dissolution of oxygen molecules into water [11] were accelerated by strong gradient static magnetic fields.

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In the precedent studies described above, strong inhomogeneous static magnetic fields were produced using an electromagnet in the early studies [2,7] or superconducting magnets in the more recent studies [1,3,4,8-11]. The product of the magnetic flux density and its gradient and the magnetic susceptibility determine the magnetic force acting on paramagnetic materials. Although the magnetic field produced by a strong permanent magnet is weaker than that produced by superconducting magnets, the magnetic field gradient very close to the magnet is comparable to the magnetic field gradient of superconducting magnets. Therefore, we have presumed that oxygen existing very close to a strong permanent magnet can be affected by the steep gradient magnetic field. This study investigated the control of dissolved oxygen concentration in a homogeneous solution using magnetic forces attributable to the gradient of strong magnetic fields near a Nd-Fe-B permanent magnet. Absorbance of copper complex produced by

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a following reaction with oxygen was measured with a spectrophotometer to elucidate the oxygen concentration change.

$$2Cu + O_2 + 2H_2O + 8NH_3 = 2[Cu(NH_3)_4]^{2+} + 4OH$$

## 2. Materials and methods

# 2.1. Tetraamminecopper(II) complex-producing reaction

A Nd-Fe-B permanent magnet (98 mm × 98 mm × 35 mm) with 0.63 T maximum magnetic flux density was placed under a Petri dish filled with 15 ml of 10% ammonia water. The Petri dish (diameter: 90 mm, depth: 15 mm, thickness of base plate: 1.4 mm) was made of polystyrene. The opening of the Petri dish was uncovered. Fig. 1 shows that a copper sheet  $(80 \text{ mm} \times 10 \text{ mm} \times 0.40 \text{ mm})$  was placed on the center of the Petri dish. The Petri dish and the magnet were positioned in a closed plastic box  $(30 \text{ cm} \times 32 \text{ cm} \times 50 \text{ cm})$  which was stored in an incubator at 288 K and the reacted solutions, producing tetraamminecopper(II) complex, were measured respectively using a spectrophotometer at 580 nm wavelength after 0, 30, 60, 90, 120, 150, 180, 240, 300, and 360 min. The least amount of oxygen consumed by the tetraamminecopper(II) complex production was then calculated. In addition, reference samples using a wooden plate instead of the permanent magnet were prepared.

To evaluate the relationship between the solution depth and the effect of magnetic fields, the Petri dishes were filled respectively with 10% ammonia water of 10, 12.5, 15, 20, 25, 30, and 40 ml; then they were respectively placed on the magnet and stored at 288 K for 180 min. The tetraamminecopper(II) complex production in the reacted solutions was examined. Moreover, the influence of ammonia concentration was examined with ammonia water of 2.5%, 5%, 7.5%, 10%, 12.5%, 15%, 17.5%, 20%, 22.5%, and 25%, respectively.



Fig. 1 shows that a midpoint of one side on the northpole surface of the permanent magnet is defined as the origin of a rectangular coordinate system. Three-dimensional magnetic flux densities near the magnet were determined using a Hall effect magnetometer (Model HGM-8200; ADS Co., Ltd., Tokyo, Japan). The handle of its probe (Type F-1, active area of 0.165 mm  $\times$  0.165 mm) was fixed on a micromanipulator. The active area of the probe was positioned near the magnet by operating the micromanipulator. The magnetic flux densities were measured around the magnet, stepwise 2.0 mm. Gradients of the magnetic flux densities are calculated from the measured values of the magnetic flux densities.

## 3. Results and discussion

The copper complex producing reaction consists of at least the following two steps: (1) Cu ion producing process regarding with dissolved oxygen, and (2) tetraamminecopper(II) complex-producing process. Some copper ions will make coordinate bonds with aqua molecules co-instantaneously. However the ligand of hydrate copper-complex will rapidly be replaced with ammonia because ammonia has a stronger coordinate capability according to Werner's coordination theory [12]. The first step of the reaction must be the copper ion production step caused by copper oxidization, and then copper complex is produced. Therefore, the concentration of the produced tetraamminecopper(II) complex is related to the dissolved oxygen consumed.

The least amount of oxygen consumption can be calculated by the amount of tetraamminecopper(II) complex production. Fig. 2 shows the relationship between reaction



Fig. 1. Schematic diagram of the experimental setup. A Nd–Fe–B permanent magnet (98 mm  $\times$  98 mm  $\times$  35 mm) with 0.63 T maximum magnetic flux density was placed under a Petri dish (diameter: 90 mm, depth: 15 mm, thickness of base plate: 1.4 mm) filled with ammonia water. A copper sheet (80 mm  $\times$  10 mm  $\times$  0.40 mm) was placed on the center of the Petri dish. The north-pole was the top face (*x*–*y* plane).



Fig. 2. Relationship between reaction time and concentration of the tetraamminecopper(II) complex in 15 ml of 10% ammonia water (depth is 2.36 mm). Error bars represent standard deviations (n = 3).

time and amount of tetraamminecopper(II) complex production. The production amount with the magnetic fields gradient is greater than that without the magnetic field gradient after 150 min. Moreover, this enhancement of the reaction rate caused by the magnetic field gradient increases with reaction time. The least amount of oxygen consumption is approximately 1.8 mg in the 15 ml of ammonia solution after 150 min, which initially contains dissolved oxygen of approximately 120 µg. The dissolved oxygen concentrations in 14% ammonia water in a 200 ml beaker sealed with a 500 ml bottle were measured with a DO meter (D-25, Horiba, Kvoto, Japan) to confirm the initial dissolved oxygen concentration (data not shown). Then it is indicated that the dissolved oxygen concentration reaches a steady-state after three days and that it is almost the same as that of water in natural weather, i.e. 8 mg/l. The required oxygen amount is much more than the initial amount of dissolved oxygen in the solution.

Fig. 3 shows the relationship between ammonia concentration and amount of tetraamminecopper(II) complex production. Enhancement attributable to the magnetic field gradient increases with the ammonia concentration of 10-20%. Then it is constant at greater than 22.5%. For that reason, ammonia is not excess for reactions at less than 20%, and ammonia concentration influences the rate in this range.

Fig. 4 shows the relationship between depth of the solutions and the amount of tetraamminecopper(II) complex production. The initial amount of dissolved oxygen is insufficient for the reaction, oxygen-dissolving step. Therefore, oxygen transfer from air to the solution is important in these conditions. Fig. 4 shows a nonlinear curve dependent on the distribution of dissolved oxygen related with



Fig. 3. Relationship between ammonia concentration and concentration of tetraamminecopper(II) complex production in 15 ml of ammonia water after 180 min (depth is 2.36 mm). Error bars represent standard deviations (n = 3).



Fig. 4. Relationship between depth of the solutions and concentration of tetraamminecopper(II) complex production. Error bars represent standard deviations (n = 3).

the relationship between diffusion and consumption rates of oxygen molecules. The same tendency of the concentration increase with decrease of depth is observed also in the control case, because the diffusion distance is reduced. Nevertheless, the difference between the result under the magnetic field and that of the control increases dramatically at a height less than 2 mm from the bottom of the Petri dish (i.e. less than 3.4 mm from the surface of the magnet). Therefore, the attraction force working on oxygen molecules in the air, such as the magnetic force, might affect this phenomenon.

Fig. 5 shows the magnetic flux densities near the magnet; the product of the magnetic flux density and its gradient were calculated. The magnetic body force per volume f (N/m<sup>3</sup>) was calculated as follows [13]:

$$\mathbf{f} = -\frac{\mu_0}{2} H^2 \nabla \kappa_{\rm m} + \frac{\mu_0}{2} \nabla \left( H^2 \frac{\partial \kappa_{\rm m}}{\partial \rho} \rho \right) \tag{1}$$

where  $\mu_0$  (H/m) is the vacuum permeability, H (A/m) is magnitude of magnetic field,  $\kappa_m$  (dimensionless) is the relative permeability, and  $\rho$  (kg/m<sup>3</sup>) is the density of oxygen gas. As the magnetic flux density  $\mathbf{B} = \mu \mathbf{H}$  (T), the magnetic permeability  $\mu = \mu_0(1 + \chi_v) = \mu_0\kappa_m$ , and  $\nabla \times \mathbf{H} = 0$ , Eq. (1) can be rewritten as

$$\mathbf{f} = \frac{\chi_{\mathbf{v}}}{\mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B} \tag{2}$$

where  $\chi_v (=1.8 \times 10^{-6})$  is the volumetric magnetic susceptibility of oxygen gas. Both  $\chi_v$  and  $\mu_0$  are constant. Therefore, the magnetic force is directly proportional to  $(\mathbf{B} \cdot \nabla)\mathbf{B}$ . The maximum value of the product  $|(\mathbf{B} \cdot \nabla)\mathbf{B}|$  was 44 T<sup>2</sup>/m, which was four times larger than that of an electromagnet study [7] that showed redistribution of the dissolved oxygen concentration. That value was only one order smaller than those of previous superconducting



Fig. 5. Magnetic flux densities **B** at y = 0 (a) and  $|(\mathbf{B} \cdot \nabla)\mathbf{B}|$  at y = 0 (b). The center of the copper sheet was placed on x = y = 0 and z = 1.4 mm attributable to the thickness of the Petri dish.

magnet studies that demonstrated the diffusion process of dissolved oxygen molecules in water [8–10] and dissolution process of oxygen molecules into water [11].

To find the magnetic force per molecule of  $O_2$ ,  $\chi_v$  is divided by the number of molecules per volume. For  $O_2$  gas at 288 K and 1 atmosphere the number of molecules per volume is  $2.5 \times 10^{25}$  m<sup>-3</sup>. Therefore, the magnetic susceptibility per molecule  $\chi$  of  $O_2$  is  $7.1 \times 10^{-32}$  m<sup>3</sup>. Using  $\chi$ , the magnetic gradient force on an  $O_2$  molecule  $F_m$  (N) is given by

$$\mathbf{F}_{\mathbf{m}} = \frac{\chi}{\mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B} \tag{3}$$

Fig. 6 shows the vertical magnetic force  $F_{mz}$  acting on an oxygen molecule depending on the height from the bottom of the Petri dish. At a depth of less than 2.6 mm the vertical magnetic force was greater than  $5.2 \times 10^{-25}$  N of the grav-



Fig. 6. Vertical magnetic force acting on an oxygen molecule on x = y = 0.

itational force for an oxygen molecule. The magnetic force increases at a depth of less than 2.6 mm and increases dramatically at a depth of less than 0.6 mm. The enhancement of difference between the result under the magnetic field effect and that of the control in Fig. 4 shows a similar tendency to increase dramatically at a height of less than 2 mm. A comparison of Figs. 4 and 6 shows that greater enhancement of the reaction rate occurs when the stronger force works on an oxygen molecule.

### 4. Conclusion

Chemical reactions involving dissolved oxygen in solution are controllable using the magnetic field gradient of a permanent magnet. The respective maximum values of magnetic flux density and the product of the magnetic flux density and its gradient were 0.63 T and 44  $T^2/m$ . When the solution depth is less than 2.6 mm and the magnetic field effect is sufficient, oxygen molecules in the air are attracted by the magnetic field gradient, thereby enhancing the reaction of the tetraamminecopper(II) complex production remarkably.

This applied technique enables control of the rate of a chemical reaction involving oxygen in a microreactor. Further study is necessary to develop control methods for chemical reactions using permanent magnets.

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