Numerical Formulation of Pigment Release from Magnetically Anisotropic Gel Beads with Respect to the Magnetic Moment in an Alternating Magnetic Field

Yasuzo SAKAI, Mitsuyoshi KUWAHATA, and Fujio TAKAHASHI*
Department of Applied Chemistry, Faculty of Engineering,
Utsunomiya University, 2753 Ishiimachi, Utsunomiya 321
(Received June 3, 1991)

Quantitative measurements were carried out regarding the change of pigment release ($\Delta C_P/C_P$) from magnetically anisotropic gel beads (MA gel beads) prepared in the presence and absence of an alternating magnetic field in various conditions. The rate of pigment release from the MA gel beads was found to be proportional to the magnetic moment of the beads. The magnetic moment of the MA gel beads was proportional to the concentration of ferrite (C_F) and the strength of a static magnetic field (H_S) used for the preparation of the MA gel beads. In this connection, M_1/V was proportional to $C_F \cdot H_S$, where M_1 and V are the magnetic moment and the volume of a grain of the MA gel beads, respectively. As a result, we derived an experimental equation for the rate of pigment release as a functions of M_1, V and the strength of an alternating magnetic field (H_A) as $\Delta C_P/C_P = kM_1H_AV^{-0.5}$, where k is constant.

It has been reported that magnetite-containing gel beads in a fluidized bed can be stirred by applying a magnetic field from outside in order to facilitate an enzyme reaction.[1,2] However, the studies showed no results for the oscillation of gel beads in an alternating magnetic field, since the gel beads did not exhibit a magnetically anisotropic property. There have been many papers concerning magnetic orientation of retinal rod outer segments[3,4] and crystals of lecithin.[5,6] There was no description of oscillation except for the orientation of particles.

It was reported in previous papers that a gel beads formed in a static magnetic field from a solution of alginate or κ-carrageenan dispersing ferromagnetic powder exhibited a property of magnetic anisotropy.[7,8] These magnetically anisotropic gel beads (MA gel beads) were found to oscillate in an alternating magnetic field. Molecular transfer through the surface of the MA gel beads was accelerated by the oscillation of the beads. It was thought that the rate of molecular transfer might depend on the magnitude of the magnetic moment of the MA gel beads. Hence, the influence of the magnetic moment on the oscillation of (and on the molecular transfer through the surface of) MA gel beads was investigated quantitatively. This paper presents an experimental equation derived from results that showed the rate of pigment release from alginate MA gel beads changed proportionally with respect to the magnetic moment due to the presence and absence of an alternating magnetic field in various conditions.

Experimental

Alginate MA gel beads containing Sr-ferrite were prepared by the established method.[7] The measurement of the release rate of toluidine blue O from MA gel beads was carried out with the same equipment including a column, an electromagnetic coil, a transformer (at 50 Hz), an inverter (at more than 50 Hz), a function generator and an amplifier (at less than 50 Hz), and under the same experimental conditions, as described in the previous paper.[7] The column effluent was fractionated, and the concentration of toluidine blue O (C_P) in each effluent fraction was determined by measuring the absorption with a spectrophotometer. The symbol, ΔC_P, was expressed as the difference between the toluidine blue O concentration before and after exposure to a magnetic field.

The magnetic moment of a grain of the MA gel beads (M_1) was determined with the modified torsion balance method equipped with two Helmholz coils. In order to measure M_1, several particles of MA gel beads, which were suspended with a string of phosphor bronze, were placed in the line of coaxis of the Helmholz coil. The long axis of the sample turned because of torque after exposure to the magnetic field. The angle of torsion, ϕ, was measured by balancing the torque in the magnetic field against the torsion generated in the string of phosphor bronze. It was presumed that ϕ was proportional to the torque, which was equal to a product of the magnetic moment (M) and the strength of the magnetic field generated by the Helmholz coil (H). Accordingly, the magnetic moment could be expressed as follows:

$$M = k'\phi/H, \tag{1}$$

where k' is a constant with regard to the torsion of the string of phosphor bronze in our experiment. The value of k' was determined by a magnetite-containing anisotropic agar gel, the magnetic moment of which was determined from measuring the moment of inertia and the period of oscillation by a vibration magnetometer in the magnetic field generated by the Helmholz coil.

Results and Discussion

The Effects of the Magnetic Properties of Ferromagnetic Powder on $\Delta C_P/C_P$. Different sizes, shapes and magnetic propeties of ferromagnetic powders including γ-Fe_2O_3 and Sr-ferrite were examined with regard to the relationship between $\Delta C_P/C_P$ and the magnetic moment of unit volume (m). MA gel beads were prepared with 5% Sr-ferrite and under 1600 Oe (1 Oe=1000/4π A m^{-1}) of a static magnetic field. The measurement of $\Delta C_P/C_P$

was carried out under 600 Oe of an alternating magnetic field. A larger $\Delta C_P/C_P$ was found to result from a stronger residual magnetization of ferrite. A typical result is shown in Table 1, which indicates that $\Delta C_P/C_P$ of MA gel beads depends on the different magnetic properties of the ferrite powder. Consequently, we used the ferrite powder which exhibited the strongest residual magnetization in our stock.

The Effect of a Static Magnetic Field and Ferrite Concentration on the Magnetic Moment of MA Gel Beads. The magnetic anisotropy of the gel beads was considered to correspond to the magnetic moment. Therefore, the effect of the strength of the static magnetic field used for the preparation of the MA gel beads (H_S) on the magnetic moment, and the effect of the concentration of ferrite in the MA gel beads (C_F) on the magnetic moment were examined in order to estimate the magnetic anisotropy of the gel beads. The results are shown in Fig. 1. It was found that m $(=M_1/V)$ was directly proportional to C_F with constants H_S. On the other hand, m was found to increase proportionally with H_S in the region of $H_S<2500$ Oe, and reached a plateau in the region of $H_S>3000$ Oe, when C_F was constant.

Table 1. The Relationship between $\Delta C_P/C_P$ and M_1 of MA Gel Beads Containing Various Ferromagnetic Powders

Ferromagnetic powder	A	B
Residual magnetization/emu g^{-1}	12	37
Coercive force/Oe	1600	2500
Volume of a grain of MA gel beads (V)/cm^3	7.9	8.1
Magnetic moment of a grain of MA gel beads (M_1)/emu	0.009	0.041
Magnetic moment of unit volume (m)/emu cm^{-3}	1.2	5.1
$\Delta C_P/C_P$	0.17	0.82

H_A=600 Oe, H_S=1600 Oe, C_F=5 %.

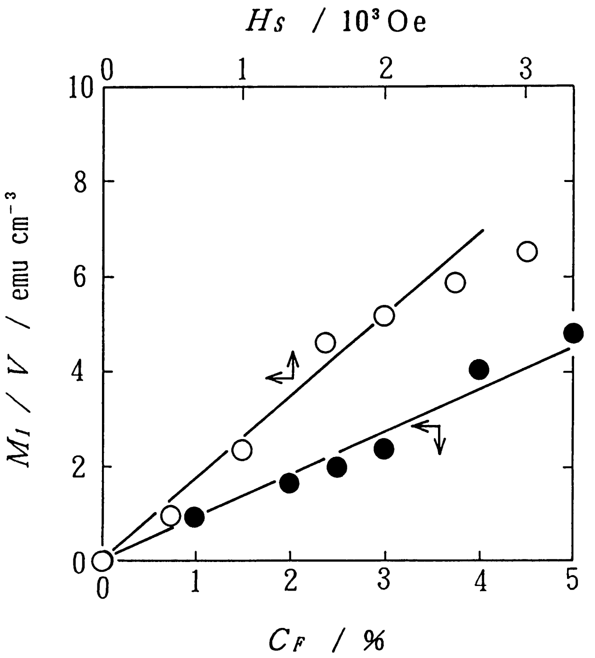

Fig. 1. The effect of H_S and C_F on m $(=M_1/V)$. —○—: C_F=5%, V: 1.91—16.1$\times10^{-3}$ cm^3. —●—: H_S=1600 Oe, V: 1.91—14.0$\times10^{-3}$ cm^3.

As expected from the previous papers,[7,8] the results of Fig. 1 indicated that m was related to both C_F and H_S for the preparation of MA gel beads. From each slope of the straight lines in the cases of H_S=1600 Oe and C_F=5% in Fig. 1, we obtained,

$$M_1/V=9.0\times10^{-1}\,C_F, \tag{2}$$

$$M_1/V=2.6\times10^{-3}\,H_S. \tag{3}$$

Eq. 2 should include the factor H_S. In order to express H_S, the constant in Eq. 2 could be replaced by $9.0\times10^{-1}/1600=5.6\times10^{-4}$ emu cm^{-3} %$^{-1}$ Oe^{-1}. The constant in Eq. 3 was calculated to be $2.6\times10^{-3}/5=5.2\times10^{-4}$ emu cm^{-3} %$^{-1}$ Oe^{-1} in the same way. Both agree within experimental error. Therefore, Eqs. 2 and 3 could be rearranged to the following equation with the average constant 5.4×10^{-4} emu cm^{-3} %$^{-1}$ Oe^{-1}:

$$M_1/V=5.4\times10^{-4}\,C_F\,H_S. \tag{4}$$

It was concluded from Eq. 4 that the magnetic moment, which depended on the magnetic anisotropy of the gel beads, was proportional to both C_F and H_S used in the preparation of the MA gel beads.

The Relationship between $\Delta C_P/C_P$ and the Magnetic Moment of a Grain of the MA Gel Beads. The movement of MA gel beads resulted from the action of magnetic torque in an alternating magnetic field. MA gel beads moved freely in the column and their movements were very complicated due to a combination of inversion, rotation, and translation. Accordingly, it is difficult to discuss the magnetic torque of the MA gel beads in relation to the relative velocity between the surface of the MA gel beads and the surrounding solution. On the other hand, the results in previous papers suggest that the velocity change of pigment release might correspond to $\Delta C_P/C_P$.[7,8] Therefore, it was useful to determine the velocity change of pigment release from the MA gel beads with respect to the magnetic moment or the size of the MA gel beads.

The effect of the magnetic moment on $\Delta C_P/C_P$ was examined by using equal-sized MA gel beads. When the ferrite concentration was changed in Figs. 1 and 3, α-Fe_2O_3, which is not ferromagnetic, was added into the MA gel beads to make a constant total concentration of ferrite and α-Fe_2O_3, so that the specific gravity of the MA gel beads might be kept constant. The results are shown in Figs. 2 and 3. Straight lines were obtained by using same-sized MA gel beads in plots of $\Delta C_P/C_P$ against M_1. The slope of each line decreased when using larger-sized MA gel beads. It was thought that the smaller the size of the MA gel beads, the stronger the oscillation with the same magnetic moment, since the

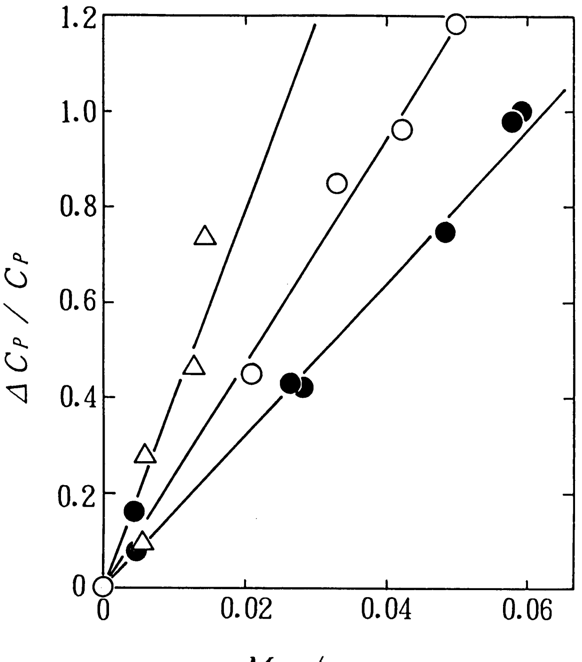

Fig. 2. The effect of M_I on $\Delta C_P/C_P$ with respect to H_S. C_F=5%, H_A=600 Oe (50 Hz). H_S: 0—2500 Oe. —△—: V=2.5, —○—: V=7.2, and —●—: $V=13.4\times10^{-3}$ cm^3.

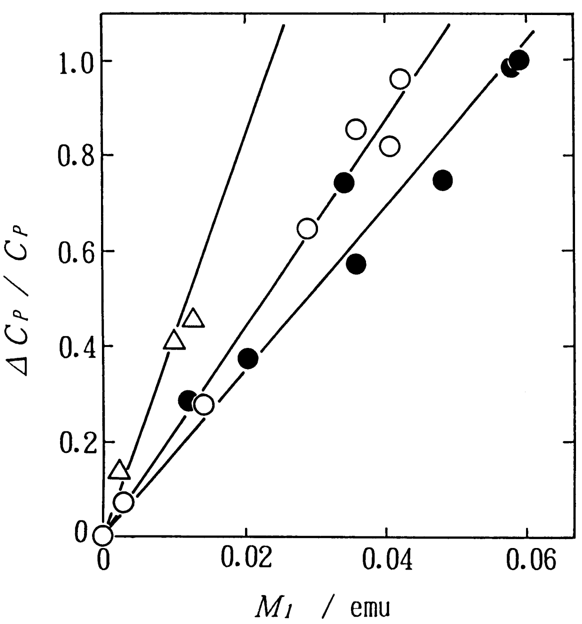

Fig. 3. The effect of M_I on $\Delta C_P/C_P$ with respect to C_F. H_S=1600 Oe, H_A=600 Oe (50 Hz). C_F: 0—5 %. —△—: V=1.8, —○—: V=7.4, and —●—: $V=13.8\times10^{-3}$ cm^3.

magnitude of the oscillation corresponded to $\Delta C_P/C_P$. It was concluded that the velocity of pigment release increased proportionally to M_I with same-sized MA gel beads.

The relationship between $\Delta C_P/C_P$ and the volume of a

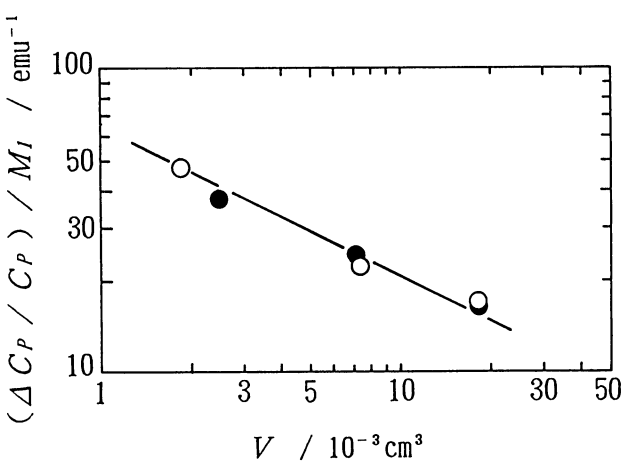

Fig. 4. The relationship between $(\Delta C_P/C_P)/M_I$ and V. —●—: Slopes in Fig. 2 and —○—: Slopes in Fig. 3.

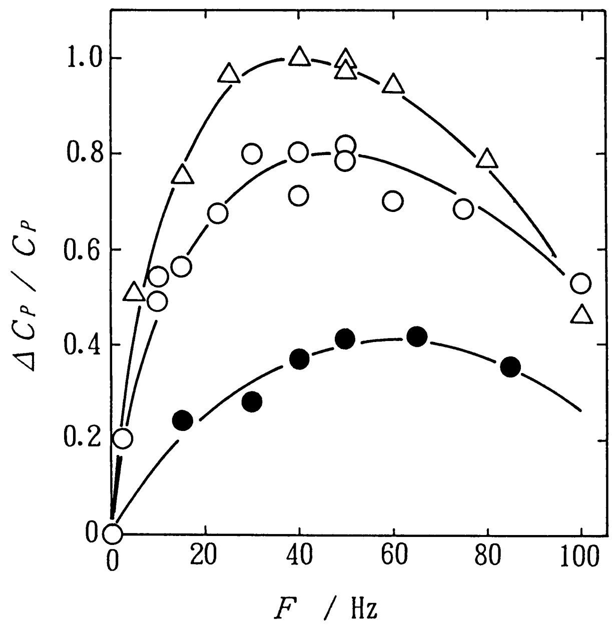

Fig. 5. The relationship between $\Delta C_P/C_P$ and the frequency of an alternating magnetic field. H_A=600 Oe. —△—: 14.0 and 0.0089, —○—: 8.5 and 0.037, and —●—: 1.9 and 0.058 with respect to M_I/emu and $V/10^{-3}$ cm^3.

grain of the MA gel beads (V) was surveyed graphically. Plots of the logarithm of the slope of each line $(\Delta C_P/C_P)/M_I$ in Figs. 2 and 3 against the logarithm of V were found to fall on a straight line as shown in Fig. 4. From Fig. 4, the following experimental equation was obtained:

$$\Delta C_P/C_P = 1.9\ M_I\ V^{-0.5}. \tag{5}$$

All results of M_I were obtained at 600 Oe of an alternating magnetic field. It has been reported that $\Delta C_P/C_P$ is proportional to the strength of an alternating magnetic field (H_A).[7] The constant in Eq. 5 should include a factor with respect to H_A. In order to add H_A to Eq. 5, the constant was changed from 1.9 to 1.9/600=3.2×10^{-3} emu^{-1} Oe^{-1} cm$^{-1.5}$. As a results, Eq. 5 was improved as follows:

$$\Delta C_P / C_P = 3.2\times10^{-3}\ M_1\ H_A\ V^{-0.5}. \tag{6}$$

The Effect of the Frequency of an Alternating Magnetic Field on $\Delta C_P/C_P$. Since the oscillation of the MA gel beads resulted from the change of the magnetic polarity with time in the alternating magnetic field, $\Delta C_P/C_P$ was expected to increase with increasing frequency of the alternating magnetic field. The relationship between $\Delta C_P/C_P$ and the frequency of an alternating magnetic field of 600 Oe gave curves as shown in Fig. 5. Smaller MA gel beads brought about a lower $\Delta C_P/C_P$ due to a smaller magnetic moment. Each curve gave a maximum point. It seems that MA gel beads may oscillate with the highest rate at the maximum frequency in Fig. 5. The maximum point of each curve shifted to a lower frequency when V became larger. This fact suggested that smaller MA gel beads might easily follow the change of the magnetic polarity in the alternating magnetic field: When the frequency of the alternating magnetic field is too high, MA gel beads might be unable to follow the change of the magnetic polarity because the moment of inertia of the MA gel beads might delay the movement.

The Conclusive Experimental Equation on the Rate of Pigment Release from MA Gel Beads. It was suggested that the constant in Eq. 6 may be influenced by various conditions for the preparation of the MA gel beads such as C_F, H_S and so on. Also, it was expected that k was influenced by the shape and specific gravity of the MA gel beads, and the viscosity of the solution in which the MA gel beads oscillate. Therefore, it was better to generalize Eq. 6 as,

$$\Delta C_P / C_P = k\ M_1\ H_A\ V^{-0.5}, \tag{7}$$

where k is constant.

Eq. 7 is a very elegant equation, and will be useful in determining the intensity of the oscillation of MA gel beads. However, some questions remain. We can not at present speculate as to why $\Delta C_P/C_P$ is proportional to the square root of V.

References

1) E. Sada, S. Katoh, and M. Terashima, *Biotech. Bioeng.*, **22**, 243 (1980).

2) E. Sada, S. Katoh, and M. Terashima, *Biotech. Bioeng.*, **23**, 1037 (1981).

3) M. Chabre, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 5471 (1978).

4) F. T. Hong, D. Mauzerall, and A. Mauro, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 1283 (1971).

5) I. Sakurai, Y. Kawamura, A. Ikegami, and S. Iwayanagi, *Proc. Natl. Acad. Sci. U.S.A.*, **77**, 7232 (1980).

6) F. T. Hong, *J. Colloid Interface Sci.*, **58**, 471 (1977).

7) Y. Sakai, H. Taguchi, and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **62**, 3207 (1989).

8) Y. Sakai, M. Kuwahata, and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **63**, 2358 (1990).