Effects of pulsating magnetic fields on electrolytic mass transfer around cylindrical cathodes

EFFECTS OF PULSATING MAGNETIC FIELDS ON ELECTROLYTIC MASS TRANSFER AROUND CYLINDRICAL CATHODES

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The influence of pulsating magnetic fields on mass transfer was studied experimentally in the electroreduction of ferrocyanide ions around an inclined cylindrical cathode under diffusion-controlled conditions. The mass transfer rate is increased by applying the pulsating magnetic field as well as the static one. The time-averaged enhancement of the mass transfer rate is dependent markedly on duty cycle (ON-time ratio), peak magnetic flux density of the applied pulsating magnetic fields in a range of 20 to 200 mHz, and slightly on its frequency. The mass transfer coefficient was correlated well by two types of non-dimensional regression equations with and without a duty-cycle factor, by using the "magneto-diffusion factor" to express the contribution of the applied magnetic flux density.

Introduction

Studies on magnetochemistry have been made since the 1930s, as shown in early reviews (Steiner and Ulrich, 1989; Tanimoto, 1989). Among research subjects, electrochemical reaction rates are known to increase or decrease by applying a magnetic field. This phenomenon is interpreted as follows: the MHD flow induced by the magnetic field accelerates or hinders the development of the hydrodynamic boundary layer around an electrode, depending on the direction of the applied magnetic field (Iwakura *et al.*, 1984a); this directly results in the enhancement or depression of mass transfer between the bulk solution and the electrode interface.

Many investigations have been made to observe the flow pattern induced by the MHD effect around electrodes with different geometries (Mohanta and Fahidy, 1976; Quraishi and Fahidy, 1980; Kim and Fahidy, 1989). Quantitative studies on the MHD flow generated around an electrode are almost nonexistent to date (O'Brien and Santhanam, 1987).

Research on electrolytic mass transfer in a magnetic field has focused on vertical flat plates or rotating discs. Furthermore, enhancement data of the mass transfer rate due to the MHD effect are known to be difficult to obtain a suitable correlation equation (Fahidy, 1990).

Most recently, the magnetoelectrolytic mass transfer around spherical and inclined cylindrical cathodes, which are more practical geometries, was studied experimentally in the horizontal or vertical magnetic field (Mori *et al.*, 1994a and 1994b). The mass transfer coefficient obtained

was correlated effectively by introducing the "magneto-diffusion factor."

All of the above investigations on mass transfer rate of magnetoelectrolysis pertain to the effect of a static magnetic field. The influence of the time variation of an imposed magnetic field on the mass transfer rate has seldom been dealt with to date. By applying a magnetic field with sinusoidal perturbation, an impedance technique was developed to interpret the dynamics of the magneto-electrolysis (Aaboubi *et al.*, 1990).

In the present report, the effect of pulsation of applied magnetic flux on the mass transfer rate in diffusion-controlled magnetoelectrolysis around an inclined cylindrical cathode is studied experimentally for a $K_3Fe(CN)_6$-$K_4Fe(CN)_6$ system. The mass transfer coefficient obtained is time-averaged and correlated to obtain a dimensionless regression equation including a parameter for the duty cycle (ON-time ratio), by introducing the magneto-diffusion factor.

1. Experimental Set-up and Method

By using electrolytic reduction of $Fe(CN)_6^{3-}$ ion, experiments were performed with a supporting electrolyte on a cylindrical cathode surface and the mass transfer rate was measured by the limiting current technique. The essential configuration of the electrolytic cell used in the experiments, fundamental procedures, and preparation for the experiments are similar to that in the previous works (Mori *et al.*, 1994a and 1994b), except for those related to measurements of periodical changes in electrolytic current and magnetic flux density, as mentioned later. The setup of experimental apparatus is schematically

① Electromagnet
② Electrolytic cell
③ Gaussmeter
④ Potentiostat
⑤ Amplifier
⑥ Recorder
⑦ Power supply unit
⑧ Function generator
⑨ Oscilloscope
⑩ Clock counter
⑪ Personal computer
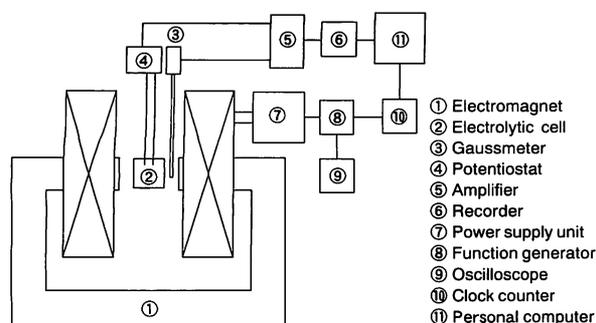
Fig. 1-A Schematic diagram of experimental apparatus
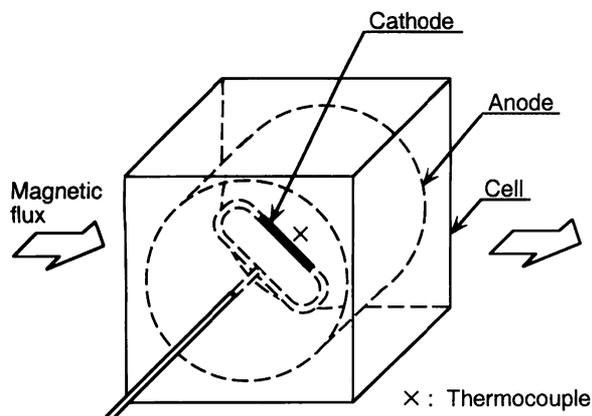
Fig. 1-B Details of electrolytic cell

shown in **Figs. 1-A** and **1-B**.

An electrolytic cell with inside dimensions of 50 mm square × 40 mm long was made of acrylic resin plate and the platinum anode of a short circular duct, 45 mm in diameter × 30 mm long, was set so as to surround the cathode. The cylindrical platinum cathode, 10.3 mm long and 1.99 ± 0.02 mm in diameter, was located in the center of the cell, so that the anode and cathode axes intersect each other at right angles. The inclination angle of the cathode axis was specified as $\theta = 0$, $\pi/6$ or $\pi/3$ rad from the horizon on a plane parallel to the magnetic field.

A pulsating magnetic field was applied in the horizontal direction, which was generated by supplying a direct electric current of rectangular wave to an electromagnet from a power supply unit (Tamaoki Electronics Co. Ltd., TE-PULSE-1200K) controlled by a function generator (Iwatsu Electric Co. Ltd., FG-330).

The electric current for the electrolysis was supplied by a potentiostat at 0.3 V cell voltage which gave a diffusion-controlled limiting current under any specified magnitude of static magnetic flux density for each cathode configuration.

The electrolyte was 0.15 M equimolar aqueous solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ with 1.0 M NaOH. The exact concentration of $Fe(CN)_6^{3-}$ was determined by spectrophotometry.

All the experimental runs were carried out at 23.0 ± 0.2 °C.

The specified voltage was applied to the cell when

the charged electrolyte solution was stationary at constant temperature. After the steady state was attained, a limiting current in free convection was recorded by an autograph recorder. Then, the pulsating magnetic field was applied at specified peak flux density and frequency. The periodical changes in the limiting current from the potentiostat and the magnetic flux density from a gaussmeter with a Hall effect probe were recorded for one period in a standing oscillation on a personal computer. Herein, an amplifier and a multi-channel A/D converter were employed and the data sampling was synchronized with the signal from the function generator. Finally the magnetic field was switched off and the resulting value of limiting current was reconfirmed to be the same as that of the initial free convection.

The above procedure was repeated for different peak magnetic flux densities, up to $B_p = 250$ mT at an interval of 50 mT, duty cycles of the pulse (ON-time ratio in one cycle); $D_Y = 0.2, 0.5$ and 0.8, frequencies; $f = 20, 80, 140$ and 200 mHz, and inclination angles of the cathode; $\theta = 0$, $\pi/6$ and $\pi/3$ rad. At a frequency higher than $f = 200$ mHz with $D_Y = 0.2$, the induced peak magnetic flux density could not reach a specified value. Under a frequency much lower than 10 mHz, the transient behavior had returned to a steady state of free convection by the end of one cycle.

The mass transfer coefficient was calculated from the observed limiting current, I, by the following relation.

$$k = I / (zAFC) \tag{1}$$

The enhancement of mass transfer rate is evaluated on the basis of the rate under the same experimental conditions except the magnetic field as

$$k_M / k_0 = I_M / I_0 \tag{2}$$

where the subscripts M and 0 imply values with and without the magnetic field, respectively.

2. Results and Discussion

The effect of cell size was examined by preliminary experiments under the conditions without magnetic field, to ensure that the case of a cylindrical cathode in the cell with the anode of circular duct shape is similar to that in infinite space. The mass transfer coefficients obtained at different inclination angles were compared with the following empirical correlation for free convection mass transfer around a horizontal cylinder in electrodeposition of copper (Schütz, 1963).

$$Sh_0 = 0.53 Ra^{1/4} \qquad (1.2 \times 10^7 < Ra < 10^9) \tag{3}$$

When $(d/\cos\theta)$ is employed as the characteristic length in the Sh and the Ra numbers instead of the cylinder diameter, this equation is applicable to an inclined cylinder (Nippon Kikai Gakkai, 1965). The experimental data
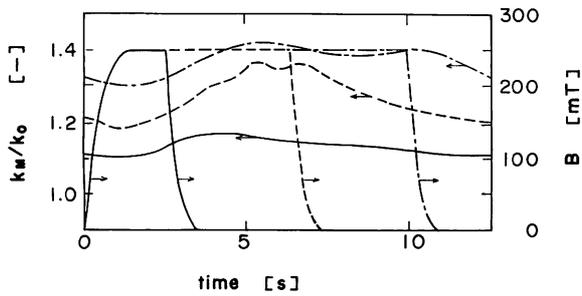
Fig. 2 Applied periodic magnetic fields and the resultant enhancement of mass transfer coefficient during one cycle (solid lines: $D_Y = 0.20$, broken lines: $D_Y = 0.50$, dash-and-dot lines: $D_Y = 0.80$)
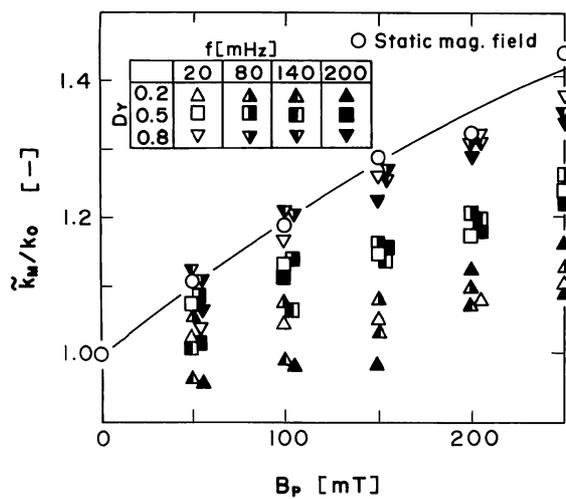
Fig. 3 Averaged enhancement of mass transfer coefficient against peak magnetic flux density ($\theta = 0$ rad)

agreed well with Eq.(3), with slight deviation showing that the effect of cell size is negligible under simple free convection.

2.1 Enhancement of mass transfer

Figure 2 shows typical time variations of observed magnetic flux density and resulting instantaneous enhancement of mass transfer, k_M/k_0, during one cycle for different duty cycles, under the conditions of $f = 80$ mHz, $B_p = 250$ mT and $\theta = 0$ rad.

Excitation of the electromagnet was like a first-order delay element with time constant, about 1/3 s. This is the reason why the induced peak magnetic flux density does not reach a specified value for a frequency higher than $f = 200$ mHz with $D_Y = 0.2$ as mentioned above.

The resultant time course of the enhancement of the mass transfer is not so regular as the applied magnetic field is. A large time-lag is observed in each enhancement curve, compared to the magnetic flux density. For $D_Y = 0.2$, the curve is comparatively monotonic, but secondary periodic fluctuations appear in the curves for the higher duty cycles.

The instantaneous enhancement of mass transfer coefficient shown in Fig. 2, is averaged over the entire cycle
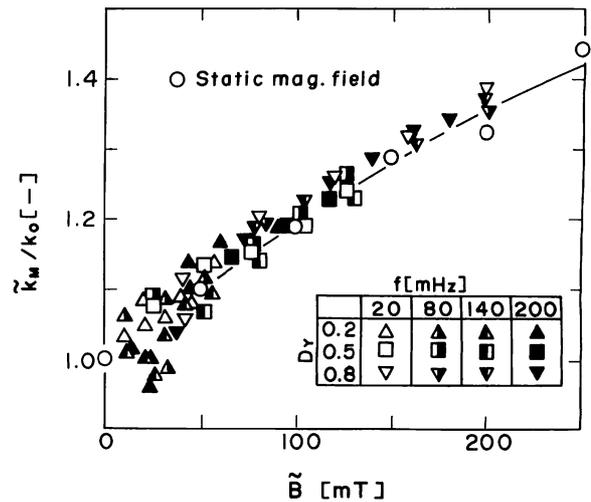
Fig. 4 Averaged enhancement of mass transfer coefficient against averaged magnetic flux density ($\theta = 0$ rad)

as follows:

$$\tilde{k}_M / k_0 = 1 / (k_0 T) \int_0^T k_M (t) \, dt \qquad (4)$$

The obtained average enhancement data, $\tilde{k}_M/k_0$, are plotted in Fig. 3 against applied peak magnetic flux density, B_p, with the parameters of frequency and duty cycle, for the case of $\theta = 0$ rad, compared with the data for the static magnetic field. Generally the averaged enhancement increases non-linearly with the applied magnetic flux density, as well as those for the static magnetic field in previous studies (Mohanta and Fahidy, 1974; Iwakura et al., 1984b; Fahidy, 1990; Chopart et al., 1991), but decreases with decreasing duty cycle. Although the influence of the magnetic field frequency is not so clear as that of the duty cycle, the enhancement seems to decrease slightly with an increase in frequency. As a whole, applying a pulsating magnetic field is found to be not so effective under the conditions of high f and low D_Y.

Although results for $\theta = \pi/6$ and $\pi/3$ rad are omitted here, the dependency of the averaged enhancement on each parameter is generally very similar to that in Fig. 3. But in the very low B_p region, the enhancement is rather small and depression of the mass transfer even occurs for $\theta = \pi/3$ rad in the higher f region. In the lower D_Y region, the enhancement dependency on the frequency tends to be unstable.

The averaged enhancement of mass transfer is essentially dependent on the amount of energy required to generate a magnetic field; i.e, representatively the product of the duty cycle and the peak magnetic flux density, B_pD_Y. Since the induced magnetic field does not behave as an exactly rectangular wave due to the time-lag effect, as shown in Fig. 2, we estimated an average magnetic flux density over one cycle instead of B_pD_Y as follows:

$$\tilde{B} = (1 / T) \int_0^T B_p (t) \, dt \qquad (5)$$

The averaged enhancement of mass transfer, $\tilde{k}_M/k_0$,

is re-plotted in **Fig. 4** for $\theta = 0$ against such averaged magnetic flux density, $\tilde{B}$, instead of the peak value, B_p.

It is found that all the experimental data show good clustering around those for the static magnetic field. The data obtained mainly for $D_Y = 0.2$ tend to scatter around the result for the static magnetic field.

Although the results are omitted here, also for $\theta = \pi/6$ and $\pi/3$ rad, the data are similarly well clustering around those for the static magnetic field in comparison with the correlation against B_p. Data clustering is rather poor and unstable under conditions of high frequency and low duty cycle, suggesting different behavior.

To further understand the mechanism of the above mentioned unstableness, and to clarify the characteristics of the secondary periodic change in the time course of the enhancement, the Fourier analysis was performed for the instantaneous data as shown in Fig. 2. Comparison of the obtained power spectra for different experimental conditions revealed the following: generally the intensity of the fundamental component predominates over the spectrum and no characteristic resonance is observed; the intensities of the higher-order harmonic components tend to increase in the high frequency range with a small duty cycle of the applied magnetic field, but no positive influence appears in enhancement of the mass transfer rate. We could not find, however, any characteristic behavior of the enhancement related quantitatively with the given experimental conditions through the Fourier transform analysis.

2.2 Dimensionless correlation of experimental data

As mentioned in the previous section, the averaged enhancement of mass transfer shows a behavior similar to that for the static magnetic field if the intensity of the applied pulsating magnetic field is represented by a magnetic flux density averaged during one period. Therefore, an attempt is made to correlate the averaged mass transfer coefficient in a similar manner to that for the static magnetic field by introducing the following magneto-diffusion factor (Mori *et al.*, 1994a) derived from the normalization of the governing differential equations.

$$M_D = zF\tilde{B}\Delta C \,(d \,/\, \cos\theta)^2 \,/\, (\rho v) \tag{6}$$

where the averaged magnetic flux density $\tilde{B}$ and the inclination angle θ of the cylindrical cathode are simultaneously taken into account.

The Sherwood number is plotted against $M_D Ra^{1/2}/Sc$ in **Fig. 5**, following the procedure in the previous study (Mori *et al.*, 1994a) and compared with the experimental correlation equation, Eq. (7), for a cylindrical cathode in the horizontal static magnetic field.

$$Sh_{MS} = 2.72 \,(M_D \, Ra^{1/2} \,/\, Sc)^{0.244}$$
$$\text{for } 5.68 \times 10^2 \le M_D \le 2.29 \times 10^5,$$
$$\text{and } 1.31 \times 10^5 \le Ra \le 6.08 \times 10^7 \tag{7}$$

In the graph, the frequency of the magnetic field f is employed as a parameter but the influence of f is seen to
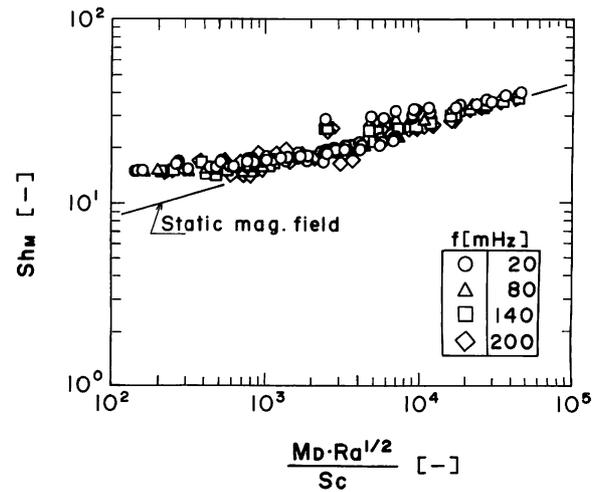
Fig. 5 Correlation of averaged mass transfer coefficient by using magneto-diffusion factor

be negligibly small. Generally the Sh_M number tends to approach asymptotically Eq. (7) as $M_D Ra^{1/2}/Sc$ increases. Equation (7) seems to be a fairly good expression for the pulsating magnetic field, including the effect of the cathode inclination and the duty cycle. However, the data tend to deviate substantially from Eq. (7) and approach a constant value for each f as $M_D Ra^{1/2}/Sc$ decreases. The major data points in this deviated region are for $\tilde{B} < 50$ mT. Under such a weak magnetic field, the effect of natural convection will probably predominate the mass transfer. Consequently the other appropriate regression equation will be needed to take more properly into account the influence of the natural convection.

Now, the magnetic field employed for the present experiments is periodically pulsating, i.e., turned ON and then turned OFF. In the ON-state the mass transfer rate will be represented by Eq. (7) and in the OFF-state by Eq. (3). In other words, the combination of Sh_{MS} from Eq. (7) and Sh_0 from Eq. (3) would give a good expression for the present data. Conventionally, the following regression equation is often used for dealing with transport phenomena affected simultaneously by two different mechanisms (Mohanta and Fahidy, 1976).

$$Sh_M{}^n = Sh_0{}^n + Sh_{MS}{}^n \tag{8}$$

In this study, the above relation is modified so as to add the duty cycle as the weight. That is

$$Sh_M{}^n = \{(1 - D_Y) \, Sh_0\}^n + \{D_Y \cdot Sh_{MS}\}^n \tag{9}$$

We applied Eq. (9) to the present data and obtained the best fit at $n = 1$, namely the linear combination of Eqs. (3) and (7) accompanied with the weight of the duty cycle, with the correlation coefficient 0.975. Thus

$$Sh_M = (1 - D_Y) \, Sh_0 + D_Y \cdot Sh_{MS} \tag{10}$$

The correspondence of the experimental data, Sh_{EXP}, to the left hand side of Eq. (10), Sh_{CAL}, is shown in **Fig. 6** with the frequency as a parameter. From this graph, Eq. (10) is shown to be a good expression of the experimental data,
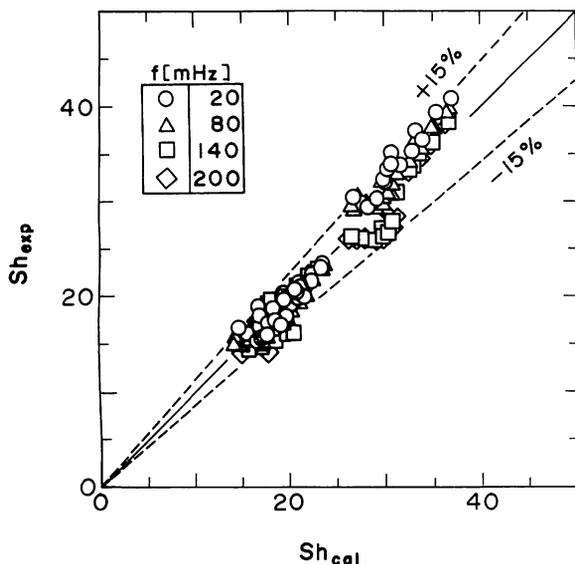
Fig. 6 Correspondence between experimental Sherwood number and that calculated from Eq. (10)

even for the small $\tilde{B}$ region within an error of ±15 %. The data in the higher range, which are for $\theta = \pi/3$, seem to show comparatively poor clustering.

Conclusions

Enhancement of the mass transfer rate around an inclined cylindrical cathode by applying a pulsating magnetic field in the horizontal direction was investigated experimentally for a $K_3Fe(CN)_6$-$K_4Fe(CN)_6$ system with supporting electrolyte, NaOH, by using the limiting current technique.

The mass transfer coefficient was found to be readily increased by applying a pulsating magnetic field as well as a static one. The enhancement data, however, scatter to increase or to decrease in the low averaged magnetic flux density region, i.e., the low duty cycle region and the high frequency region. The averaged enhancement of the mass transfer increases markedly with increases in the duty cycle and the peak magnetic flux density, however, the influence of the frequency is slightly appreciable.

By using the magneto-diffusion factor, the mass transfer coefficient averaged over one period was correlated very well with the dimensionless regression equation, Eq. (10), where the duty cycle and the inclination angle of the cathode are simultaneously accounted for. The dimensionless regression equation without a duty-cycle factor, Eq. (7), for the static magnetic field correlates fairly well with the present data by replacing the static magnetic flux density with the time-averaged value of the pulsating one. The influence of the frequency of the applied magnetic field on the mass transfer coefficient disappears by employing the magnetic flux density averaged over one cycle to represent the intensity of the magnetic field.

Further research is required to find out a criterion to identify whether the applied magnetic field plays a role as an enhancer or a depressor in the region of small time-aver-

aged magnetic flux density.

Nomenclature

A	=	surface area	[m^2]
B	=	magnetic flux density	[T]
C	=	bulk concentration of ion	[mol/m^3]
ΔC	=	concentration difference between bulk solution and electrode interface	[mol/m^3]
D	=	diffusion coefficient	[m^2/s]
d	=	diameter of cylindrical cathode	[m]
D_Y	=	duty cycle, i.e., ON-time ratio in one cycle	[-]
F	=	Faraday constant	[C/eq.]
f	=	frequency	[Hz]
g	=	gravity acceleration	[m/s^2]
Gr	=	Grashof number, defined as $g\zeta\Delta C\,(d/\cos\theta)^3/v^2$	[-]
I	=	limiting current	[A]
k	=	mass transfer coefficient	[m/s]
M_D	=	magneto-diffusion factor based on mean magnetic flux density, defined as $z\tilde{F}\tilde{B}\Delta C\,(d/\cos\theta)^2/(\rho v)$	[-]
Ra	=	Rayleigh number, defined as $GrSc$	[-]
Sc	=	Schmidt number, defined as v/D	[-]
Sh	=	Sherwood number, defined as $\tilde{k}\,(d/\cos\theta)/D$	[-]
T	=	period of pulsation	[s]
t	=	time	[s]
z	=	valency of ion	[eq/mol]
ζ	=	densification factor	[m^3/mol-1]
θ	=	inclination angle of cathode from the horizon	[rad]
v	=	kinematic viscosity	[m^2/s]
ρ	=	density	[kg/m^3]

<Subscripts>

cal	=	calculated value
exp	=	experimental data
P	=	peak value of pulsating magnetic field
M	=	with magnetic field
0	=	without magnetic field

<Superscripts>

~	=	value averaged over one cycle

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