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The Control of the Phenylglyoxylic Acid Permeation Rate through a Liquid Membrane of a Toluene–Chloroform Mixture Containing Magnetite under a Rotating Magnetic Field and an Alternating Magnetic Field

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A liquid membrane containing ferromagnetic powder (LM-FP) was proposed for controlling the molecular permeation rate through a liquid membrane in a rotating magnetic field (R-MF) in a previous paper. This paper presents details concerning the property of LM-FP under exposure to R-MF or an alternating magnetic field (A-MF). Magnetite and phenylglyoxylic acid (PGA) were used as a ferromagnetic powder and a substance for permeation, respectively. Various factors, such as the magnetite concentration in LM-FP, the intensity of the magnetic field and the number of rotations of R-MF, both of which affect the PGA permeation rate, were investigated in order to understand the behavior of magnetite powder in LM-FP. Magnetized particles of magnetite powder in LM-FP were found to rotate in R-MF, but not to move in A-MF. R-MF exerted an acceleration of the PGA permeation rate through LM-FP more than did A-MF. It is suggested that magnetized particles of magnetite powder behave as micro-magnetic stirrers in LM-FP to accelerate molecular transport. Data concerning the PGA permeation rate were simulated by assuming a concentration change of PGA in LM-FP after turning R-MF on or off. We obtained simulation curves which were in accord with the experimental results.

There have been many papers concerning wide applications of a liquid membrane containing a suitable carrier for the selective separation of gases,[1,2] optical isomers,[3] as well as the cations of alkaline metals,[4,5] alkaline earth metals,[6] and heavy metals.[7,8] Some papers have described the results concerning molecular transport in termes of the concentration gradient.[4—7,9] A liquid membrane supported in a porous film and liquid membrane comprising droplets in an emulsion might deserve to be used. The former is easier to operate with higher selectivity than the latter.[10] However, a liquid membrane supported in a porous film is not recommended for practical use because of the slow transport of molecules through the liquid membrane. It is necessary to devise a method to agitate a very thin liquid membrane supported in a porous film for the acceleration of molecular transport.

The authors have proposed a liquid membrane containing ferromagnetic powder (LM-FP), which is prepared in a hole of a vessel wall. LM-FP can be agitated by applying an external rotating magnetic field (R-MF).[11] Therefore, the acceleration of molecular transport through LM-FP was expected to be observed under exposure of R-MF.

This paper presents a detailed report of a previous paper:[11] The permeation rate of phenylglyoxylic acid (PGA) through LM-FP containing magnetite was studied under exposure of magnetic field. R-MF was compared with alternating magnetic field (A-MF). Data concerning the PGA permeation rate were simulated by assuming a concentration change of PGA in LM-FP after turning on or off the magnetic field. We obtained a simulation curve which was in accord with the experimental results.

Experimental

The same equipment and reagents were used as in a previous paper.[11] The liquid components of LM-FP consisted of 1 : 1 (v/v) toluene and chloroform mixture (T–C mixture) and various concentrations of magnetite powder. In order to prepare LM-FP, 0.3 cm^3 of a T–C mixture was filled into a hole in the bottom wall of a teflon-made cylindrical bottle (Fig. 1). Two teflon bottles (inside diameter of 16 and 32 mm) were used in the same way as described in a previous paper.[11] One was used for downward (Figs. 4—7) and another for upward (Fig. 9) permeation of PGA. A magnetization curve is shown in Fig. 2. Magnetite particles were coated with (octadecyl)trichlorosilane so that they would have affinity for the T–C mixture. The apparent sizes of the particles spread over 0.02—10 μm in diameter, since particles aggregate by themselves.

The intensity and gradient of the vertical component of R-MF at the center of LM-FP were measured by a Gaussmeter (Yokogawa, type 3251). The required number of rotations of R-MF were obtained by an AC servomotor. The number of rotations of R-MF was fixed at 1200 rpm in the case of Figs. 4—6 and 9.

A-MF was generated by a solenoid (90 mm in diameter) with an AC power supply. The LM-FP was located at the center of the solenoid.

The PGA concentration in the source phase was 67 mmol dm^{-3}, and that in the receiving phase was measured by a conductometer (TOA, CM-30ET) connected to a recorder. The PGA permeation rate was obtained by a calculation of the finite difference of the PGA concentration. All experiments were carried out at 25 °C.

Results and Discussion

Behavior of Magnetite Powder in R-MF and A-MF. In order to directly observe the behavior of magnetite powder in a T–C mixture, a preliminary experiment was carried out in a test tube exposed to either R-MF

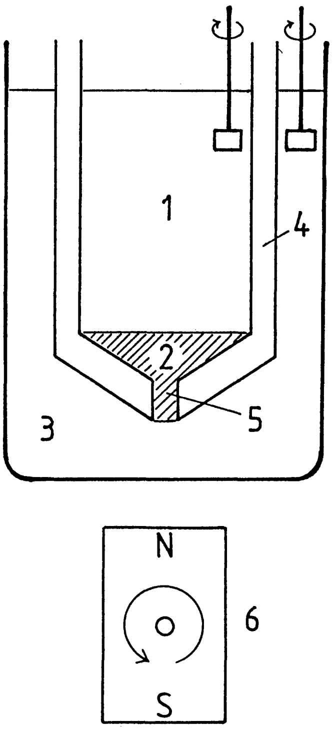

Fig. 1. Equipment of LM-FP. 1. (Downward permeation) 6 cm^3 of 67 mmol dm^{-3} PGA as a source phase, or (upward permeation) 18 cm^3 of distilled water as a receiving phase. 2. 0.3 cm^3 of LM-FP. 3. (Downward permeation) 54 cm^3 of distilled water as a receiving phase, or (upward permeation) 42 cm^3 of 67 mmol dm^{-3} PGA as a source phase. 4. A cylindrical teflon bottle (16 or 32 mm in diameter as downward or upward permeation). 5. A wall hole (1 mm in diameter, 3 mm in length). 6. Magnet.

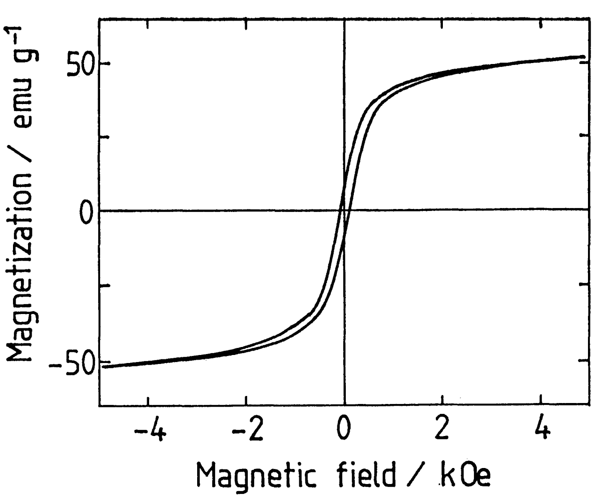

Fig. 2. A magnetization curve of magnetite powder measured with a vibration sample magnet meter.

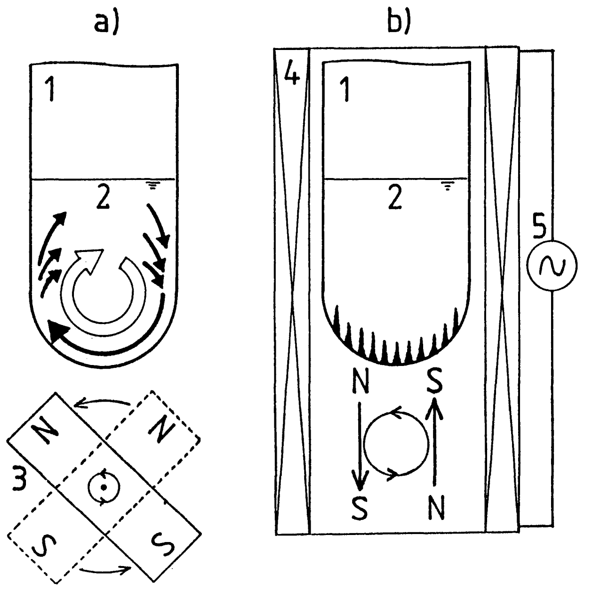

Fig. 3. The behavior of powdered particles of magnetite under exposure of R-MF and A-MF. 1. Distilled water; 2. Powdered particles of magnetite in T-C mixture; 3. Magnet; 4. Solenoid; 5. Power supply (50 Hz).

or A-MF. The movement of magnetite powder is illustrated in Fig. 3.

In the case of R-MF, magnetite powder was pulled down toward the rotating magnetic poles by both magnetic attraction and gravitation, and rotated in the direction of the arrow in Fig. 3(a). Powdered particles of magnetite were magnetized to be micromagnets in R-MF. Therefore, magnetite powder can be attracted by a magnetic force along the magnetic gradient of R-MF. Consequently, the flow of the T-C mixture occurred in the same direction (non-relief arrow in Fig. 3(a)).

In the case of A-MF, powdered particles of magnetite were observed not to move, but to align parallel to the lines of magnetic flux and to deposit at the bottom of test tube according to gravitation (Fig. 3 (b)). The A-MF exhibits properties of reversing magnetic polarity repeatedly and of actually generating no magnetic gradient. The coercive force of magnetite is so small (about 0.1 kOe (Fig. 2)) that magnetized and powdered particles of magnetite may easily change the polarity in A-MF without turning themselves. Consequently, powdered particles of magnetite were neither torqued nor moved in A-MF.

It is concluded that R-MF is effective for stirring LM-FP and, in turn, for the acceleration of molecular transport.

Effects of R-MF and A-MF on the PGA Permeation Rate. The PGA permeation rates were measured in both R-MF and A-MF. LM-FP contained 0.5% magnetite powder. A typical result is shown in Fig. 4. The PGA permeation rate increased by approximately 8 times in R-MF of 200 Oe, as compared with that in the absence of a magnetic field (Fig. 4(a)). No change in the PGA permeation rate was observed upon turning on and off the A-MF in the range between 0—420 Oe and 5—50 Hz. A typical result (200 Oe, 20 Hz) is shown in Fig. 4(b).

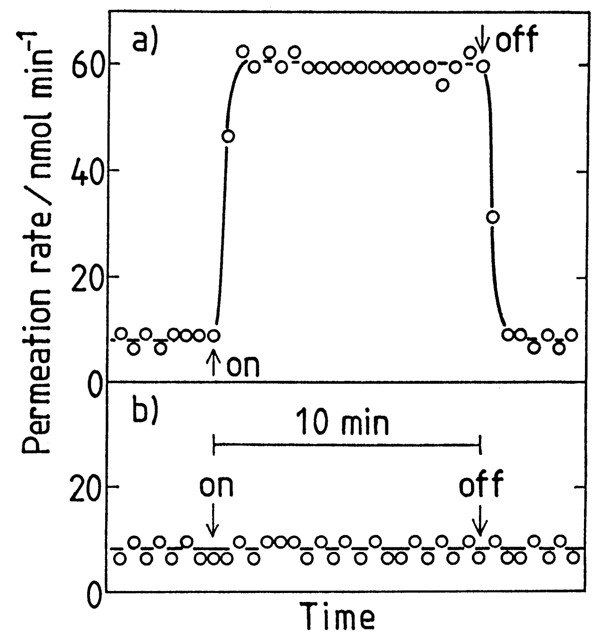

Fig. 4. The response of downward PGA permeation rate through LM-FP by turning magnetic field off and on. The LM-FP contained 0.5% magnetite powder. a) 200 Oe of R-MF (1200 rpm). b) 200 Oe of A-MF (20Hz).

The downward molecular transport at the interface of LM-FP may be accelerated by stirring the magnetite powder inside the LM-FP under exposure to R-MF. As a result, a high concentration gradient of PGA at the interface between the LM-FP and aqueous phase is generated by sufficiently stirring the LM-FP in R-MF to increase the PGA permeation rate. Judging from the result shown in Figs. 3 and 4, A-MF does not change the thickness of the diffusion layer at the interface between LM-FP and the aqueous phase.

Effect of Concentration of Magnetite Powder in LM-FP on the PGA Permeation Rate. It was expected that the PGA permeation rate might depend on the concentration of magnetite powder in LM-FP: The higher is the concentration of magnetite powder in LM-FP, the faster is molecular transport. The effect on the PGA permeation rate in the R-MF of 300 Oe was surveyed for various concentrations of magnetite powder in LM-FP. The results were compared with that in the absence of a magnetic field, as shown in Fig. 5. The PGA permeation rate was found to increase with increasing magnetite powder in the range less than 1%. A strong magnetic attraction (which was obtained in more than 1% of magnetite powder in LM-FP) was found to break the liquid membrane in R-MF.

Deposites of magnetite powder were observed in the downside interface region between LM-FP and the aqueous phase in the absence of a magnetic field. The effective area for PGA permeation might be reduced by deposition of magnetite powder. This is why the PGA permeation rate gradually decreases with increasing the magnetite concentration in the absence of a magnetic field.

Effect of Intensity of R-MF on the PGA Permeation Rate. The relationships between the PGA permeation rate and the intensity of R-MF were examined at various concentrations of magnetite powder (Fig. 6). Every curve was found to share the same point at

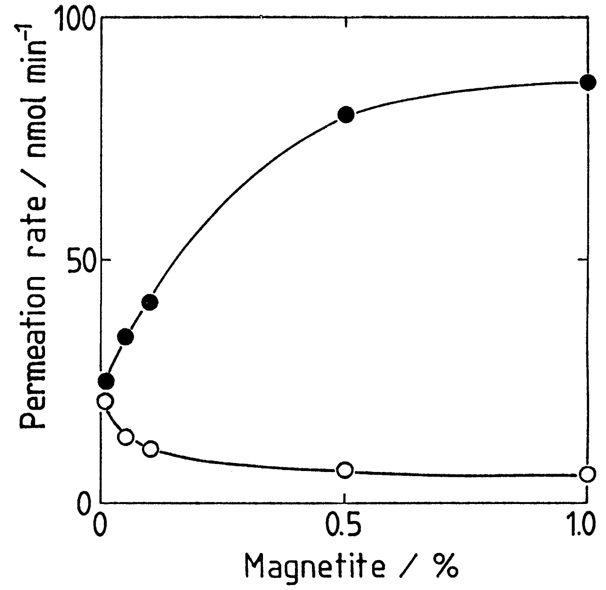

Fig. 5. The effect of magnetite concentration in LM-FP on the PGA permeation rate (downward permeation through LM-FP). Number of rotations of R-MF: 1200 rpm. —●—: 300 Oe of R-MF; —○—: No magnetic field.

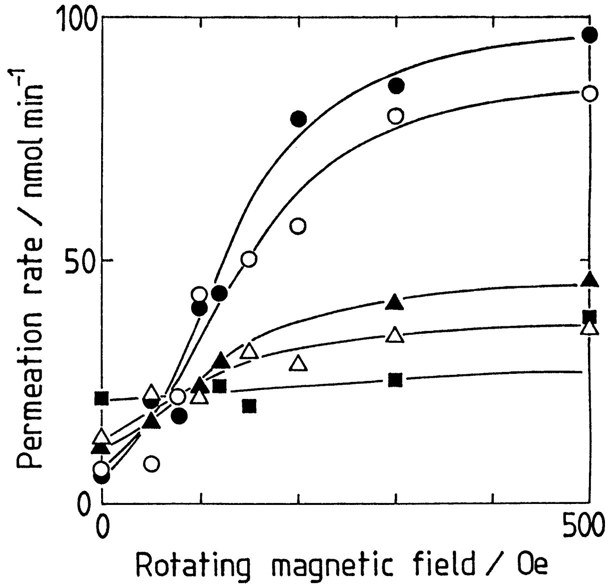

Fig. 6. The effect of intensity of R-MF on the PGA permeation rate (downward permeation through LM-FP). Number of rotations of R-MF: 1200 rpm. —■—: 0.01; —△—: 0.05; —▲—: 0.1; —○—: 0.5; —●—: 1% of magnetite powder.

about 80 Oe of R-MF.

It is reasonable that the PGA permeation rates were reduced in less than 80 Oe of R-MF, caused by the deposition of magnetite powder in the downside interface region of LM-FP (as mentioned in the previous section). In more than 80 Oe of R-MF, the effect of stirring magnetite powder seems to overcome that of depositing magnetite powder due to gravitation. In this connection, the liquid resistance of the T-C mixture should be added as one of the factors which influence the movement of magnetite powder in R-MF. It was supposed that 80 Oe of R-MF might be a threshold value for stirring magnetite powder.

Effect of the Number of Rotations of R-MF on the PGA Permeation Rate. The PGA permeation rates were determined by changing the number of rotations of R-MF. The result is shown in Fig. 7. Since magnetized particles of magnetite are easily aligned along the direction of the magnetic flux at a R-MF rotation lower than 300 rpm, the relationship between the PGA permeation rate and the number of rotations of R-MF may be expressed as a rising curve. When the number of R-MF rotations is greater than 1200 rpm, the curve increased gently to reach a plateau. The liquid resistance in LM-FP might exist against stirring magnetized powder. The number of R-MF rotation and liquid resistance, which affect the PGA permeation, might offset each other.

The Simulation of Upward and Downward PGA Permeation. Simulation curves based upon the experimental results of the PGA permeation rate were drawn using a simple model. Let the PGA permeation rate, the interface area, the volume of phase, and the PGA concentration be P, S, V and C, respectively. Both P and S are accompanied by a subscript ($_{in}$ or $_{out}$) which is expressed as the interface from the source phase to LM-FP or that from LM-FP to the receiving phase. Each subscript ($_S$, $_{LM}$, and $_R$ of C or V) indicates a source phase, LM-FP and a receiving phase, respectively. The PGA permeation rate should be proportional to both the interface area and the difference of the PGA concentration between the source phase and LM-FP (or receiving phase and LM-FP). Therefore, we defined P as a product of S and the difference of the PGA concentration. The symbols K and K^0 are constants for cases with and without a magnetic field. The subscript $_{in}$ or $_{out}$ is affixed to both K and K^0. The process of PGA permeation is illustrated in Fig. 8.

Data for upward and downward permeation given in a previous paper[11] were used for preparing simulation curves.

It is considered that C_S is a constant (67 mmol dm^{-3}) and that C_R is measurable. We should estimate C_{LM}. C_{LM}, which is zero immediately after setting the system of LM-FP in the absence of magnetic field, changes due to an inflow of PGA from the source phase to LM-FP and an outflow of PGA from LM-FP to the receiving phase with a lapse of time. C_{LM} finally reaches a constant value in the steady state. The value of C_{LM} in the absence of a magnetic field was estimated by Eqs. 1—4:

$$(P_{in})_i = K^0_{in} \cdot S_{in}\{(C_S) - (C_{LM})_i\}, \tag{1}$$

$$(P_{out})_i = K^0_{out} \cdot S_{out}\{(C_{LM})_i - (C_R)_i\}, \tag{2}$$

$$(C_{LM})_{i+1} = (C_{LM})_i + (1/V_{LM})\{(P_{in})_i - (P_{out})_i\}, \tag{3}$$

and

$$(C_R)_{i+1} = (C_R)_i + (1/V_R)\,(P_{out})_i, \tag{4}$$

where i=1, 2,.... (corresponding to every 30 seconds). When i=1, then $(C_{LM})_1$ and $(C_S)_1$ are zero. The calculation was repeated until $(C_{LM})_{i+1}$ reached the same value of $(C_{LM})_i$ by using the assumed K^0_{in} and K^0_{out}.

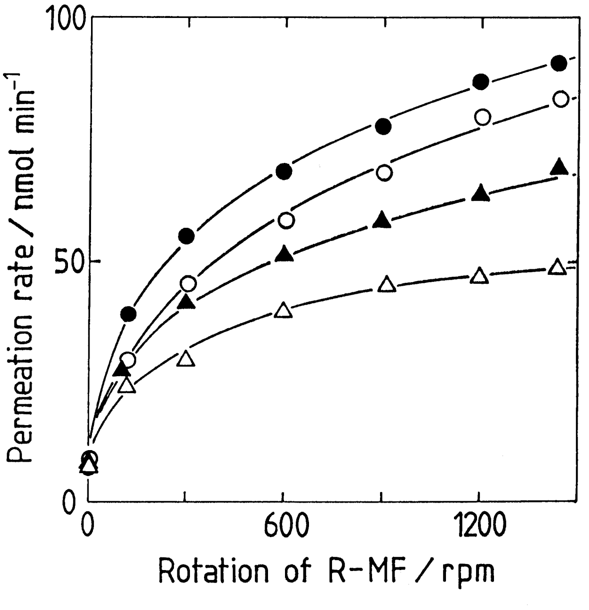

Fig. 7. The effect of number of rotations of R-MF on the PGA permeation rate (downward permeation through LM-FP). The LM-FP contained 0.5% of magnetite powder. —△—: 100; —▲—: 200; —○—: 300; —●—: 500 Oe of R-MF.

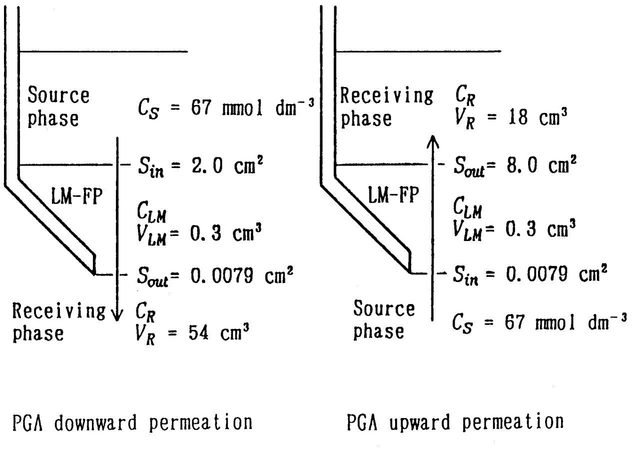

Fig. 8. The model of downward and upward permeation of PGA through LM-FP.

After turning R-MF on, K_{in} and K_{out} were used instead of K^0_{in} and K^0_{out} in Eqs. 1—2 for the caluculation of $(C_{LM})_{i+1}$ and $(C_R)_{i+1}$.

Since the upside interface area is larger than the downside one, the PGA permeation rate must be controlled mainly by PGA transport through the downside interface. In the case of downward permeation, C_{LM} may decrease rapidly to reach a certain value lower than C_S immediately after R-MF is turned on. On the other hand, C_{LM} in the case of upward permeation may gradually increase after turning R-MF on. Both values of K's were estimated for the determination of C_{LM} fitted into the experimental data by a trial-and-error method in order to make simulation curves. The results are shown in Fig. 9 and Table 1.

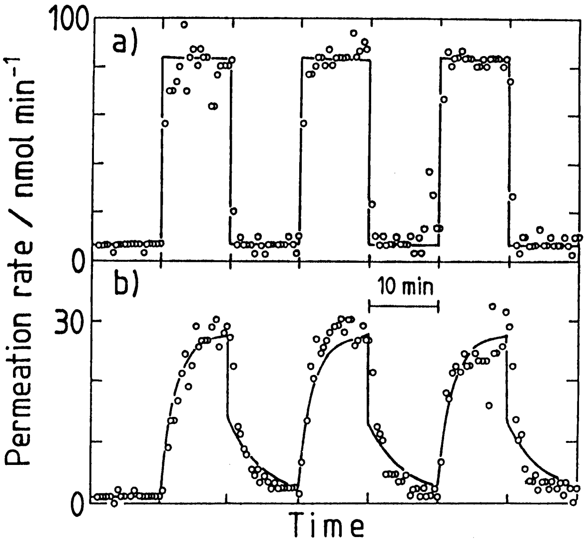

Fig. 9. The simulation curves on the downward and upward PGA permeation rates through LM-FP. The LM-FP contained 0.5% of magnetite powder. Number of rotations of R-MF: 1200 rpm. Intensity of R-MF: 300 Oe. Solid lines are the simulation curves. Plots are experimental results in the previous paper.[11] a) Downward permeation. b) Upward permeation.

Table 1. The K's Obtained by Simulation

Permeation	No magnetic field	R-MF (300 Oe)
Downward	$K^0_{in}=5.2\times10^{-5}$ $K^0_{out}=1.3\times10^{-5}$	$K_{in}=1.0\times10^{-4}$ $K_{out}=1.6\times10^{-4}$
Upward	$K^0_{out}=7.5\times10^{-6}$ $K^0_{in}=2.2\times10^{-6}$	$K_{out}=1.5\times10^{-5}$ $K_{in}=5.5\times10^{-5}$

We obtained simulation curves upon which every point of the experimental data fell. The results in Table 1 indicate that R-MF may influence the downside (smaller) interface more than the upside (larger) one.

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