

The Control of Molecular Transport Rate through Liquid Membrane  
Containing Ferromagnetic Powder under Rotating Magnetic Field

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A novel method with using liquid membrane containing ferromagnetic powder (LM-FP) under rotating magnetic field was proposed for the control of molecular transport rate through the liquid membrane. The rate of phenylglyoxylic acid transport through the LM-FP, (toluene-chloroform mixture containing magnetite powder) increased more than 10 times as compared with the transport rate under non-magnetic field.

Various methods on the application of a liquid membrane containing suitable carrier have been widely studied for the selective separation of mixtures in optical isomers,<sup>1)</sup> metal ions<sup>2-5)</sup> and gases.<sup>6)</sup> The merit of this method is that an operation of extraction and back-extraction can be carried out simultaneously at each side of both surfaces in liquid membrane. The application of this method is expected to extend into various separation of many kinds of substances such as hydrocarbons, amino acids, proteins and so on.

The rate of molecular transport through the liquid membrane might be controlled by that of diffusion inside the liquid membrane. The authors developed a new filtration instrument using a liquid-stirring membrane for the increase of the molecular transport rate, which consisted of the following: (1) The liquid membrane containing ferromagnetic powder. (2) Rotating magnet for stirring the ferromagnetic powder. We proposed this instrument as LM-FP (it means the filtration instrument with stirring liquid-membrane containing ferromagnetic powder).

This paper will present the results on preliminary studies of phenylglyoxylic acid (PGA) transport through the LM-FP in the R-MF. The LM-FP is made up of 1:1 (v/v) toluene-chloroform mixture (T-C mixture) where magnetite powder is dispersed. For the solubility in both water and T-C mixture, PGA was used as a transport reagent through the LM-FP.

The ferromagnetic powder of magnetite was prepared as follows: Into a water solution of  $\text{FeCl}_2$  and  $\text{FeCl}_3$  (the molar ratio of 1:2), NaOH solution was added to make a suspension. After heating the suspension, the precipitates were separated and washed with deionized water. The precipitates were dispersed into 1.2% sodium oleate solution at 90 °C for half an hour under stirring, and then the pH value of suspension was adjusted to pH 5.5 by adding 1 M HCl (1 M = 1 mol dm<sup>-3</sup>). The precipitates were filtered, washed with deionized water and dried up under reduced pressure at room temperature to be served as magnetite powder.

The movement of the magnetite powder was examined in two kinds of magnetic fields as preliminary experiments. The T-C mixture containing magnetite powder in a test tube was exposed in the R-MF. The R-MF was generated by rotating the cylindrical magnet attached at right angle to the spindle of the motor (Fig. 1). The frequency of the R-MF was 20 Hz. The diameter of the magnet pole is 25 mm and the residual magnetization is  $8 \times 10^3$  Gauss. The magnetite powder was observed to be pulled down to the lower part in the test tube and to be rotated by magnetic force, when the rotating magnet was placed under the test tube. Therefore, the T-C mixture was agitated by the rotation of the magnetite powder at the lower part in the test tube. On the other hand, no agitation occurred if the homogeneous alternating magnetic field (A-MF) produced by solenoid was applied to the test tube. In this case the magnetite powder was observed not to be mobile, but aligned along the magnetic flux in the A-MF. It is reasonable because the A-MF exhibits a property wherein the direction of the magnetic flux does not change, but only NS polarity of each pole changes with time alternately and there is no magnetic gradient. Consequently, the R-MF was used in this work for the agitation of the magnetite powder in the liquid membrane.

At first a preliminary experiment was carried out to confirm the PGA transport through the liquid membrane of T-C mixture.

Extraction of PGA from 67 mM PGA in aqueous solution (25 cm<sup>3</sup>) to T-C mixture (25 cm<sup>3</sup>) occurred and in turn the back-extraction of PGA from the T-C mixture to 25 cm<sup>3</sup> of water (receiving phase) followed in the same way.

As a result, the concentration of the receiving phase became 8.3 mM.

The schematic diagram of the equipment is shown in Fig. 1. A hole of 1 mm in diameter and 3 mm in depth was bored in the bottom of a teflon made cylindrical bottle (16 mm in inside diameter). This teflon bottle was inserted into a 100 cm<sup>3</sup>-jacketed beaker filled with 60 cm<sup>3</sup> of water saturated by T-C mixture. The LM-FP was prepared by putting 0.3 cm<sup>3</sup> of the T-C mixture containing 0.5% magnetite powder into the hole at the bottom of teflon bottle in the water. By this treatment, 60 cm<sup>3</sup> of water in the beaker was separated into two parts, 6 cm<sup>3</sup> of source phase inside and 54 cm<sup>3</sup> of receiving phase outside the teflon bottle. Into the source phase, 0.3 cm<sup>3</sup> of 1.33 mM PGA was added to make 6 cm<sup>3</sup> of 67 mM PGA. Both phases were stirred respectively and kept constant at 25 °C by using water jacket. The PGA concentration in the receiving phase

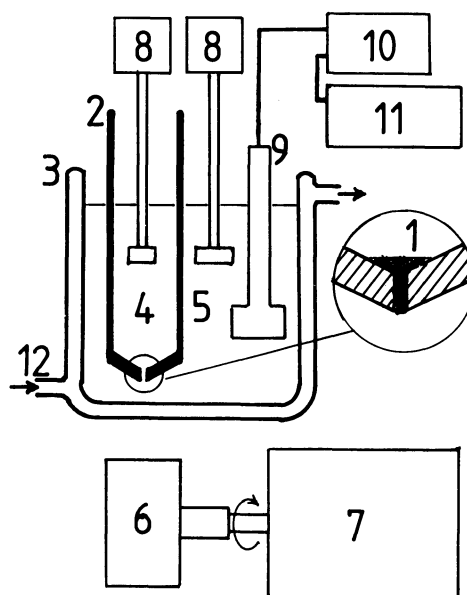


Fig. 1. The schematic diagram of equipment: (1) Liquid membrane, (2) Teflon bottle, (3) Jacketed beaker, (4) Source phase, (5) Receiving phase, (6) Magnet, (7) Motor, (8) Stirrer, (9) Conductance cell, (10) Conductometer, (11) Recorder, (12) Water jacket

was measured by a conductometer (TOA, CM-30ET), since the conductivity was confirmed to be proportional to the PGA concentration. The LM-FP was prepared and was allowed to stand during half an hour before the exposure in the R-MF for that the PGA concentration in the receiving phase was steady in an increase linearly. Then, the LM-FP was exposed in the R-MF at intervals of 10 min off and 10 min on. It was possible to turn off and on the R-MF by moving the rotating magnet far apart from or just under the beaker as shown in Fig. 1. The intensity of the magnetic flux, which was determined by a Gauss meter (Yokogawa, type 3251), was changed by shifting the rotating magnet up and down. The strength of magnetic field was expressed by cgs emu system units hereafter.

The PGA concentration in the receiving phase was plotted with the lapse of time under the R-MF of 300 Oersted on and off as shown in Fig. 2(a). The rate of PGA transport, which was obtained by the calculation of finite difference in Fig. 2(a), was shown in Fig. 2(b). The rate of the PGA transport increased about 12 times as much under the R-MF as compared to the rate without the R-MF. The other data showed that the rate of PGA transport under the R-MF of 50, 100 and 200 Oersted increased about 2, 3, and 8 times as comparing to the result without the R-MF. It should be noted that the rate of PGA transport through the T-C mixture membrane containing no magnetite powder was not influenced by the R-MF.

There might be three consecutive steps which influenced the acceleration of PGA transport through the LM-FP: (1) The agitation of the T-C mixture in the liquid membrane by rotation of magnetite powder. (2) The reduction of the thickness of diffusion layer inside the LM-FP by the agitation. (3) The increase of the PGA concentration gradient at the interface between T-C mixture and water. It is plausible that the rotation of magnetite powder may contribute to the acceleration of PGA transport at the lower side interface between T-C mixture and water. In as much as the magnetite powder is concentrated to the lower side of LM-FP due to the magnetic force and gravity. It was presumed that the rate of PGA transport at the upper side interface might have less affected than the lower side interface between T-C mixture and water.

To verify the above assumption, the direction of PGA transport was reversed by changing the setting places of PGA solution and water with each other.

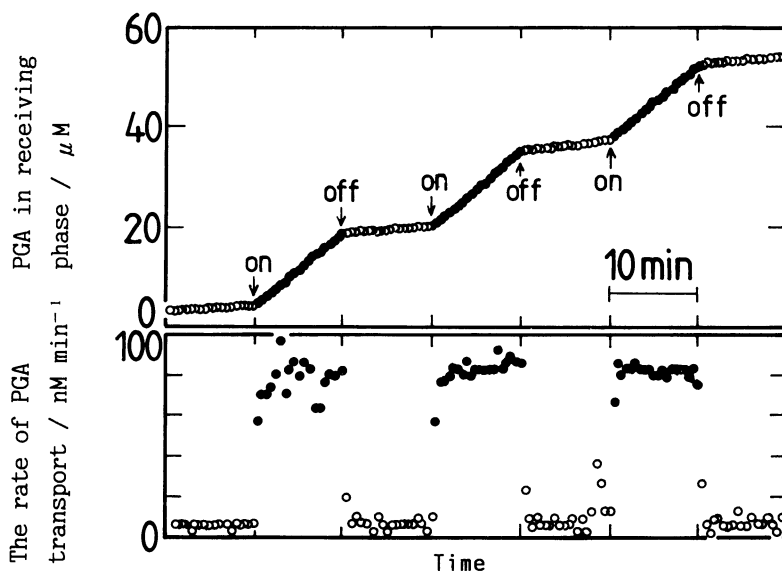


Fig. 2. Effect of the rotating magnetic field on downward transport of PGA through the LM-FP.

For this measurement, a new teflon bottle (32 mm in diameter) was used. In this case, the liquid in the beaker was separated into 42 cm<sup>3</sup> of 67 mM PGA as the source phase outside and 18 cm<sup>3</sup> of water as the receiving phase inside the teflon bottle, respectively. The LM-FP was prepared and exposed under the R-MF by the same procedure as described in the case of the downward transport of PGA. The similar results were obtained in Fig. 3, except that the rate of PGA

transport under the R-MF in Fig. 3(b) changed more slowly than that in Fig. 2(b), as was expected. It seemed to indicate in Fig. 3(b) that the PGA concentration in the LM-FP might increase in a few minutes after turning the R-MF on, and in turn the rate of PGA transport from the LM-FP to the receiving phase might also increase after short time lag.

The remarkable acceleration of molecular transport through a liquid membrane was demonstrated by the agitation of magnetite powder in the LM-FP under the R-MF. It is expected that this method will be useful for various molecular separation of mixture by the addition of suitable carrier substance in the LM-FP.

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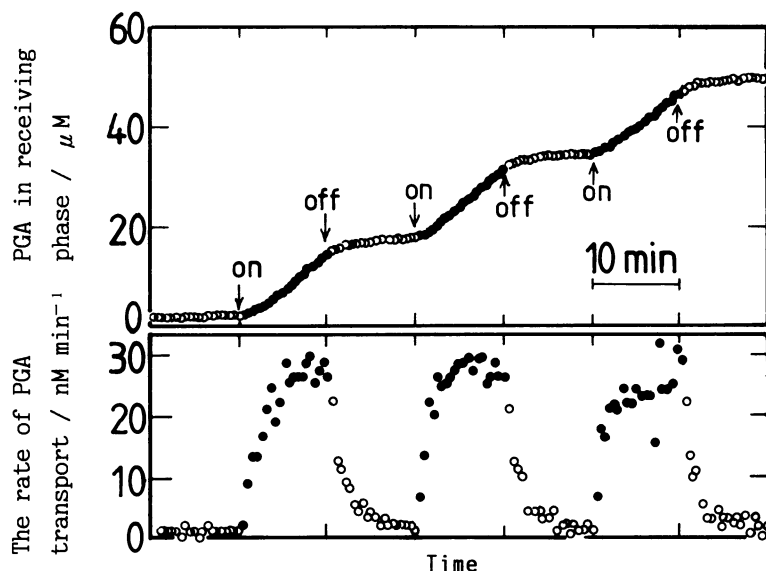


Fig. 3. Effect of the rotating magnetic field on upward transport of PGA through the LM-FP.

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