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The Selective Separation of Organic Acids through Liquid Membrane Containing Ferrite in the Presence of Alternating Magnetic Field

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The selective separation of phenylglyoxylic acid (PGA) from a mixture of PGA and mandelic acid (MA) was carried out by using a liquid membrane containing ferromagnetic powder (LM-FP) in the presence of an alternating magnetic field (A-MF). Ferromagnetic powder, which exhibits a strong coercive property, was added into a mixture of toluene and chloroform (T–C mixture). Many holes of 0.7 mm in diameter were bored in the bottom wall of a Teflon® cylindrical bottle, in which the total hole area occupied 8%. A T–C mixture containing ferromagnetic powder was filled into the holes to prepare LM-FP. Under an exposure of A-MF (200 Oe, 50 Hz) over a 12 h. Fifty four % PGA and 8% MA in the source phase were found to permeate through the LM-FP-containing Sr-ferrite from the source phase of an equimolar mixture of PGA and MA to the receiving phase. The PGA permeation rate through the LM-FP varied over a region between 0.3 and 7.5 times higher than that through a control liquid membrane not containing any ferromagnetic powder in the presence of a magnetic field.

There have been many papers concerning molecular separation studies using liquid-membrane methods. A liquid membrane can be roughly divided into the bulk,[1,2] supported,[3,4] and emulsion types.[5,6] Although the supported type is easier for work involving higher selective separation than the emulsion type, practical use for separation cannot be realized because of the low permeation rate which depends on molecular diffusion.

It was reported in a previous paper that magenetized particles of magnetite in a liquid membrane were found to oscillate in a rotating magnetic field (R-MF), as mentioned in a previous paper, and to facilitate the transport of molecules through the liquid membrane.[7,8] Though this method was expected to be useful for molecular separation, it was technically difficult to obtain a homogeneous R-MF on a large liquid membrane. On the other hand, an alternating magnetic field (A-MF) generated by coreless coils was thought to be much easier to homogeneously expose on a large liquid membrane. Since magnetite exhibiting a weak coercive force did not move in an A-MF (as mentioned in the previous paper) various ferrites exhibiting a strong coercive force were examined for stirring the liquid membrane.

This paper discussed PGA permeation examined by the use of a liquid membrane comprising a mixture of toluene and chloroform (T–C mixture) containing ferromagentic powder in the presence of A-MF or R-MF, as well as the selective transport of phenylglyoxylic acid (Ph–CO–COOH, PGA) from a mixture of PGA and D-mandelic acid (Ph–CHOH–COOH, MA) has been examined.

Experimental

The properties of the ferromagnetic powder used are summarized in Table 1. Each ferromagnetic powder was

Table 1. Properties of Ferromagnetic Powder

	Sr-ferrite	Ba-ferrite SS-1300	Ba-ferrite SS-2200	Magnetite
Saturation magnetization $(m^2 g^{-1})$	69	53	52	59
Coercive force (Oe)	3700	420	870	<100
Specific surface area $(m^2 g^{-1})$	—	41	27	—
Average diameter of particles (μm)	0.2—5	0.06—0.07		0.02—10
Shape	Plates	Hexagonal plates		Blocks

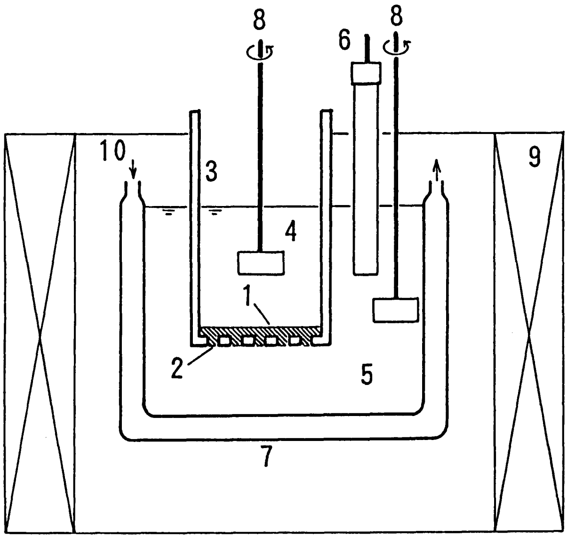

Fig. 1. Schematic diagram of the equipment. 1. LM-FP, 2. Holes, 3. Teflon® bottle, 4. Source phase, 5. Receiving phase, 6. Conductivity sensor, 7. Dual-beaker, 8. Stirrer, 9. Coreless coil, 10. Circulating water.

immersed into a toluene solution containing 20% octadecyltrichlorosilane, and then washed using toluene, and then in turn by a toluene–chloroform mixture in order to change the property of the surface of the powdered particles from hydrophilic to hydrophobic. The PGA, MA, and other chemicals used were of commercially available reagent grade.

A schematic diagram of equipment of LM-FP is shown in Fig. 1. The same Teflon® bottle in which one hole was bored at the bottom wall (described in the previous paper) was used in order to survey the optimum conditions of the species, as well as the ferrite concentration, and the intensity and frequency of the magnetic field (Figs. 2—4).

Several Teflon® cylindrical bottles (38 mm in inside diameter and 2.1 mm thick of bottom wall), the bottom walls of which were bored to make 1—224 holes of 0.7 mm in each diameter, were used as supporting vessels for the separation of PGA and MA. This Teflon® bottle was inserted into a jacketed beaker (70 mm in inside diameter). Into a jacketed beaker, 164 cm^3 of distilled water was poured, and then separated to 39 cm^3 as a source phase inside and 125 cm^3 as a receiving phase outside the Teflon® bottle (Figs. 5—7 and Tables 2 and 3).

In order to prepare LM-FP, a T-C mixture containing ferromagnetic powder was filled into the holes bored in the bottom wall of the Teflon® bottle. After removing 2 cm^3 of distilled water inside the Teflon® bottle, 2 cm^3 of a 1.3 mol dm^{-3} PGA solution, or 2 cm^3 of an equimolar mixture of PGA and MA (1.3 mol dm^{-3} each) was added into the Teflon® bottle. LM-FP was exposed in R-MF or A-MF.

PGA and MA were determined using a Shimadzu liquid chromatography instrument (LC-9A). In the case that only PGA was used in the experiment (Figs. 2—6 and Table 2), the PGA concentration was determined from the conductivity (as described in the previous paper).

A-MF was generated by supplying alternating current in a solenoid (90 mm in diameter, 145 mm in length of coreless coils). The equipment shown in Fig. 1 was placed at the center of axis of the solenoid. Various frequencies of A-MF were generated by a function generator (FG-330 of Iwasaki Tsushin) and a power supply (BWA 35-5 of Takasago) for 1—50 Hz, and a transistor inverter (VF PACK Al of Toshiba) for 50—100 Hz.

Results and Discussion

The Permeation Rate of PGA through a Liquid Membrane Containing Different Ferrites in R-MF and A-MF. Powdered ferrite particles exhibiting a strong coercive force were expected to oscillate in LM-FP due to the torque produced by A-MF. The PGA permeation rate through LM-FP, which was prepared by adding Sr-ferrite or Ba-ferrite, was determined by measuring the conductivity in the presence or absence of A-MF. A typical result is shown in Fig. 2. The PGA permeation rate was observed to respond to turning off-and-on A-MF. It is evident from the effect of A-MF that the oscillation of powdered ferrite particles facilitate PGA permeation through LM-FP.

The relationship between the PGA permeation rate and the magnetic strength in R-MF and A-MF are given in Figs. 3 and 4. R-MF, which is a non-homogeneous magnetic field, was found to facilitate PGA permeation through LM-FP, regardless of the coercive force strength of the ferromagnetic powder. It suggested that the R-MF might induce a translational motion of both the ferrite and magnetite.

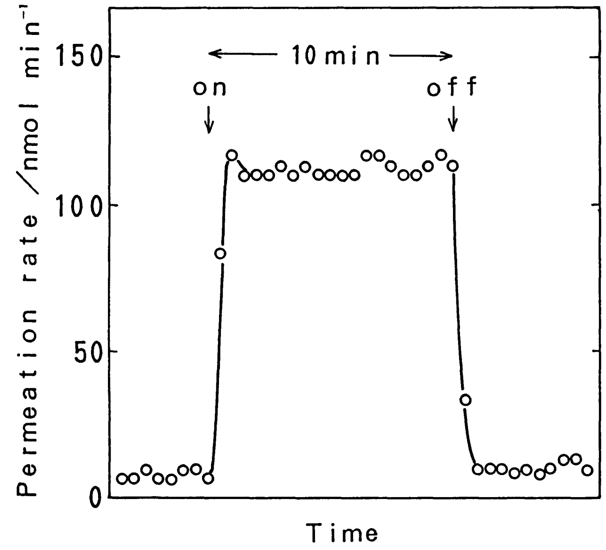

Fig. 2. Typical result of the PGA permeation rate with time in off-and-on of A-MF. The initial concentration of PGA in source phase: 67 mmol dm^{-3}. A hole of the Teflon® bottle: 0.8 mm^2 (1 mm ϕ). The inside diameter of Teflon® bottle: 16 mm ϕ. The frequency of A-MF: 50 Hz. Sr-ferrite in LM-FP: 0.5%.

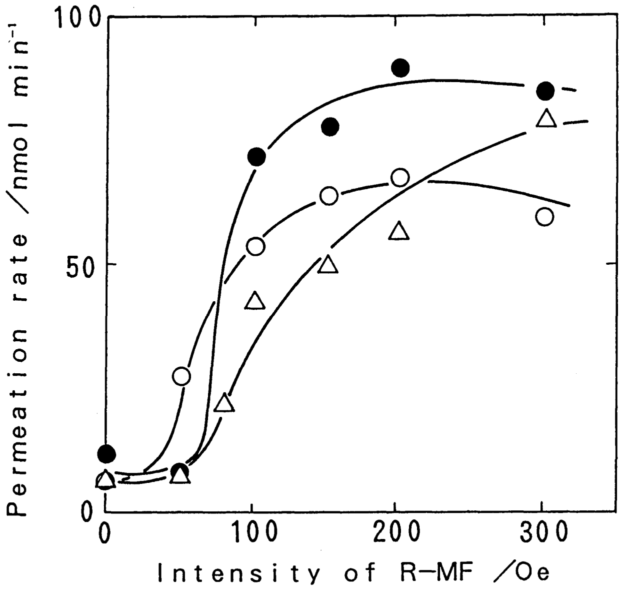

Fig. 3. Relationship between the PGA permeation rate and the R-MF intensity. The initial concentration of PGA in the source phase: 67 mmol dm^{-3}. Hole of the Teflon® bottle: 0.8 mm^2 (1 mm ϕ). The inside diameter of Teflon® bottle: 16 mm ϕ. The frequency of R-MF: 50 Hz. Sr-ferrite: —●—, Ba-ferrite (SS-2200): —○—, or magnetite: —△—in LM-FP: 0.5%.

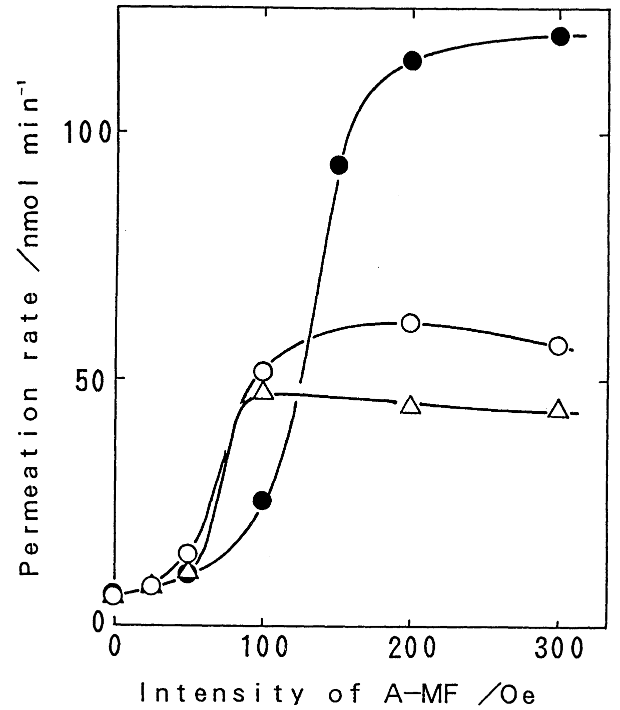

Fig. 4. Relationship between the PGA permeation rate and the intensity of A-MF. The initial concentration of PGA in source phase: 67 mmol dm^{-3}. A hole of Teflon® bottle: 0.8 mm^2 (1 mm ϕ). The inside diameter of Teflon® bottle: 16 mm ϕ. The frequency of A-MF: 50 Hz. Sr-ferrite: —●— Ba-ferrite (SS-1300): —△—, or Ba-ferrite (SS-2200): —○— in LM-FP: 0.5%.

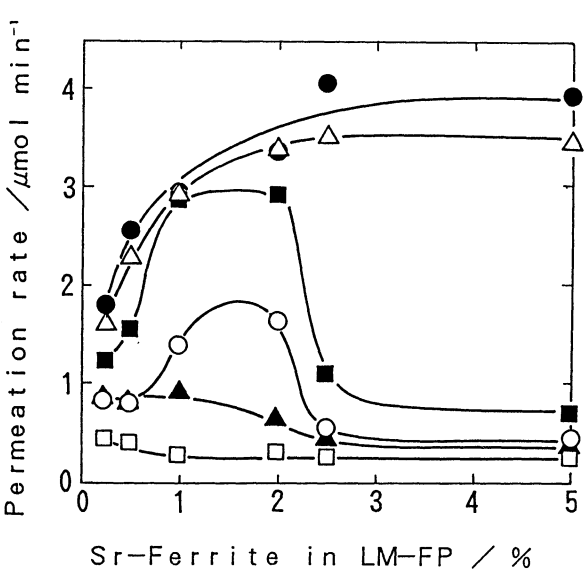

Fig. 5. Relationship between the PGA permeation rate and the Sr-ferrite concentration in A-MF. The initial concentration of PGA in the source phase: 67 mmol dm^{-3}. The total hole area of Teflon® bottle: 0.9 cm^2. The frequency of A-MF: 50 Hz. A-MF of 300: —●—, 200: —△—, 150: —■—, 100: —○—, 50: —▲—, or 0: —□—Oe.

Magnetite exhibiting a weak coercive force is known not to maintain magnetization without an external magnetic field; however, ferrite exhibiting a strong magnetic force can hold it. It is plausible that LM-FP-containing ferrite gives rise to a higher PGA permeation rate than LM-FP containing magnetite in the region of lower than 200 Oe of R-MF. (1Oe=1000/4π A m^{-1}). This is because the magnetic force is equal to the product of the gradient magnetic field strength and the magnetization of ferromagnetic powder (Fig. 4), meaning that the maximum magnetic force is dependent on the saturation magnetization of ferrite for the same strength of the external magnetic field. Consequently, a maximum PGA permeation rate was obtained in a region higher than 200 Oe for R-MF in the case of LM-FP containing ferrite.

Although the PGA permeation rate increased in A-MF through the LM-FP containing ferrite, it did not do so for magnetite (not shown in Fig. 4). The torque received by ferromagnetic powder particles is known to be proportional to with the product of the strength of A-MF and the magnetic moment of the particles. The magnetic moment is shown as a product of the volume of particles and the magnetization per unit volume. Accordingly, the result shown in Fig. 4 sustains the idea that the larger is the saturation magnetization and the particle size, the larger is the torque produced by A-MF. However, the PGA permeation rate through LM-FP containing Ba-ferrite increases in a weaker magnetic field than that for Sr-ferrite by increasing the A-MF intensity. In the case of powdered ferromagnetic particles exhibiting a strong coercive force and high magnetic moment, it is deduced that particle oscillation might be hindered in a weak magnetic field, because of the strong cohesive power between particles. Sr-ferrite, which was the best among the ferrites examined, was used thereafter for LM-FP in A-MF.

Effects of the Ferrite Concentration and Magnetic Strength on the PGA Permeation Rate. The relationship between the Sr-ferrite concentration and the PGA permeation rate is shown in Fig. 5. The PGA permeation rate increases for less than 2% Sr-ferrite, and decreases for greater than that in LM-FP upon elevating the intensity of A-MF with less than 150 Oe. Although the LM-FP was stirred by ferrite particles oscillating near the lower interface of the liquid membrane, the presence of too many ferrite particles in the liquid membrane might give rise to a decrease of the PGA permeation rate, caused by the interaction and collision between particles to hinder the motion.

The peak in Fig. 5 disappeared for an A-MF intensity of more than 200 Oe, and the PGA permeation rate reached a limit for greater than 2% of the ferrite. Ferrite particles, which oscillate intensely, tend to spring out of the holes at bottom wall, and to concentrate in the circumference region at the bottom of bottle with increasing A-MF intensity. This is because the actual concentration of ferrite in the holes may not increase in proportion to the amount of ferrite added.

Effect of the Frequency of an Alternating Magnetic Field. The effect of the frequency of A-MF on the PGA permeation rate was examined over the 0—100 Hz region at a magnetic strength of 100 Oe, and with 1% of Sr-ferrite in LM-FP. The results are shown in Fig. 6.

Since LM-FP was stirred by oscillating ferrite particles, the PGA permeation rate was thought to increase in proportion to the A-MF frequency. However, the PGA permeation rate increased rapidly in the 0—1 Hz region. It was observed that the oscillating ferrite particles not only underwent inversion but also experienced up-and-down motion due to the magnetism. The latter motion may cause a rapid increase in the PGA permeation, due to the smaller effect with inversion. The PGA permeation rate slowly increased at a frequency greater than 5 Hz. The viscosity of the liquid might give rise to some resistance and thus disturb the oscillation of ferromagnetic powder at high frequencies. This is a similar trend to that in the case of the relationship between an rpm change of R-MF and the PGA permeation rate.[8)]

Interface Area of the Liquid Membrane. Various numbers of hole were bored through the bottom wall of Teflon® bottles in order to prepare LM-FP in order to increase the PGA permeation rate. LM-FP was filled into the holes so as to make the lower interface and excess amount of LM-FP cover the entire bottom wall (11 cm^2), which is adjacent to the water phase to make the upper interface of LM-FP, inside the Teflon® bottle. We have already reported in previous papers[7,8)] that the lower interface between the water phase and LM-FP made the rate-determining step of PGA permeation through the LM-FP.

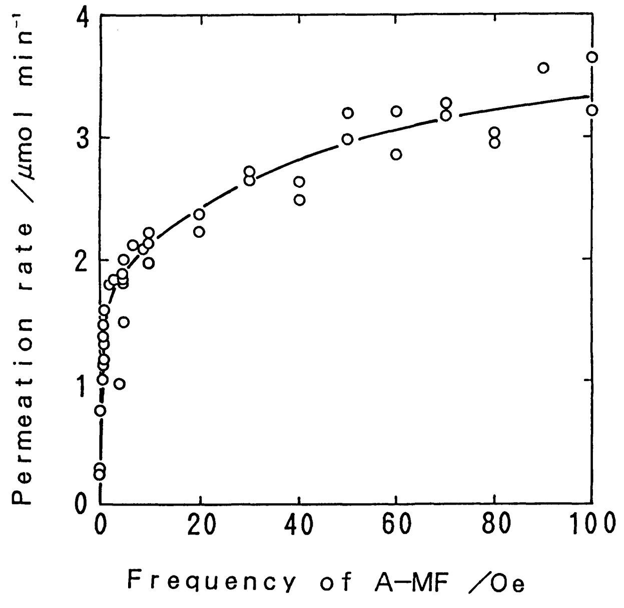

Fig. 6. Effect of the frequency of A-MF. The initial concentration of PGA in the source phase; 67 mmol dm^{-3}. The total hole area of the Teflon® bottle: 0.9 cm^2. The intensity of A-MF: 200 Oe. Sr-ferrite: 1% in LM-FP.

Each PGA permeation rate resulting from a different hole area of the bottom wall was determined with or without a magnetic field. Figure 7 shows the relationship between the size of the hole area and the PGA permeation rate in the presence of A-MF. The PGA permeation rate was found to be proportional to the area (0—0.6 cm^2).

Separation of Phenylglyoxylic Acid and D-Mandelic Acid. The different solubilities of PGA and MA into a T-C mixture was used to separate of PGA and MA. PGA, which exhibits a greater hydrophobic property than does the PGA anion, is easy to dissolve into a liquid membrane comprising a T-C mixture. The ion-

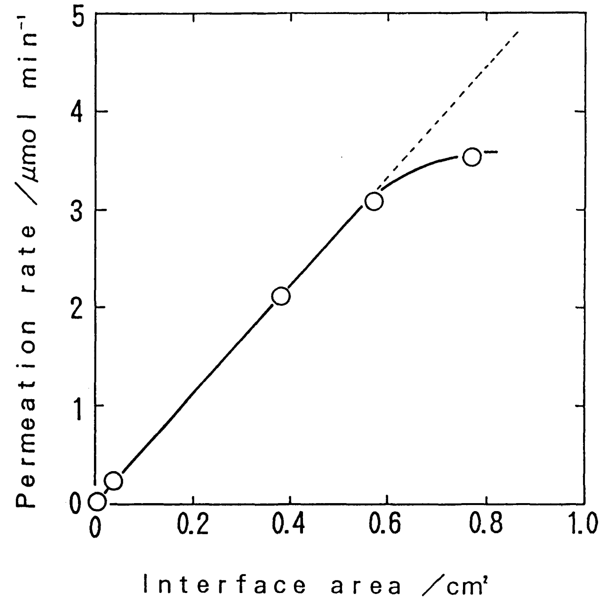

Fig. 7. PGA permeation rate with regard to the interface area of holes of the Teflon® bottle. The initial concentration of PGA in source phase (pH 1.7): 67 mmol dm^{-3}. The intensity and the frequency of A-MF: 200 Oe and 50 Hz. Sr-ferrite: 1% in LM-FP.

Table 2. pH Effect on the PGA and MA Permeation Rates

Initial pH	The permeation rate/mmol dm^{-3} h^{-1}		
	PGA	MA	PGA/MA
1.7 (source phase) (as a control)	0.105	0.017	6.2
1.3 (source phase)	0.147	0.0129	11.4
3.6 (source phase)	0.0023	0.00041	0.56
1.6 (receiving phase)	0.0109	0.028	3.9
12.6 (receiving phase)	0.056	0.015	3.7

LM-FP containing 1% of Sr-ferrite was exposed in A-MF (200 Oe, 50 Hz). The total hole area at the bottom of Teflon® bottle was 0.9 cm^2.

Table 3. Separation of PGA and MA through LM-FP

	Initial source phase (a)	After 12 h,		b/a	Separation factor, α*)
		Source phase	Receiving phase(b)		
	mmol	mmol	mmol		
PGA	2.57	1.20$^{c)}$	1.38$^{e)}$	0.54	13
MA	2.63	2.45$^{d)}$	0.21$^{f)}$	0.08	

The source phase (initial pH 1.3): 39 cm^3, the receiving phase: 125 cm^3. LM-FP containing 1% Sr-ferrite was exposed in A-MF (200 Oe, 50 Hz). The total hole area at the bottom of Teflon® bottle was 0.9 cm^2. *) $\alpha=(d\cdot e)/(c\cdot f)$.

ization degree of PGA was reduced in the presence of a strong acid. Consequently, PGA in the presence of a strong acid was expected to efficiently dissolve into the liquid membrane. On the other hand, the solubility of MA into the liquid membrane is lower than that of PGA. The pH adjustment of the source phase or the receiving phase was examined regarding the efficient separation of PGA from a mixture of PGA and MA. LM-FP containing 1% of Sr-ferrite was used under A-MF exposure (200 Oe, 50 Hz). The PGA permeation rate was obtained under various conditions, as is shown in Table 2. The highest PGA permeation rate and the best selective separation of PGA were obtained by adding a strong acid into the source phase in order to adjust the solution to pH 1.3 in the presence of A-MF.

By aiming the separation of PGA from a mixture of PGA and MA, an experiment was carried out with a Teflon® bottle having many holes bored in the bottom; the total hole area was 0.9 cm^2 in A-MF for 12 h after adding acid into the source phase to make pH 1.3. The result is shown in Table 3. The amounts of PGA and MA that permeated were found to be 1.38 and 0.21 mmol, respectively, corresponding to 54 and 8% of the respective initial amount in the source phase. The selective separation of PGA was lower than that shown in Table 2. This is reasonable, since the relative concentration of PGA in the source phase may become lower than that of MA according to higher degree of PGA transport from the source phase to the receiving phase. Consequently, the final ratio of PGA : MA in the receiving phase was obtained to be 7 : 1 from the initial mixture of PGA : MA=1 : 1 in the source phase by the permeation through LM-FP. We obtained 13 as the separation factor of PGA from a mixture of PGA and MA.

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