

$\lambda$	= latent heat of vaporization of water	[J/kg]
$\rho_G$	= density of humid air	[kg/m <sup>3</sup> ]
$\rho_L$	= density of water	[kg/m <sup>3</sup> ]

<Superscripts>

I	= tower bottom
II	= tower top
$\infty$	= steady state
	= variation

<Subscripts>

G	= air
L	= water

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# OIL-PHASE PERMEATION BEHAVIOR OF O/W EMULSION THROUGH A POROUS POLYTETRAFLUOROETHYLENE MEMBRANE

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**Key Words:** Membrane Separation, Demulsification, Permeation, Polytetrafluoroethylene, Porous Membrane, Stirred Tank

Oil-in-water emulsions consisting of drops smaller than 10  $\mu\text{m}$  were permeated through porous polytetrafluoroethylene membranes under conditions where only the oil phase permeated. Factors influencing the oil permeation flux were experimentally investigated. They are drop size, stirring velocity during the permeation experiment, volume fraction of the oil phase, and surfactant concentration, among others. When the maximum drop size was doubled, the oil flux became almost ten times larger. Effects of stirring velocity during the permeating experiment and of volume fraction of the oil phase were very large. For the case where the surfactant (SDS) concentration was 2.6 mol/m<sup>3</sup>, the oil flux was proportional to the 4th power of the stirring velocity and the 3.4th power of the volume fraction of the oil phase. As the surfactant concentration was increased up to the critical micelle concentration, the oil flux decreased to a very small value.

## Introduction

The demulsifying process of emulsions composed of very small drops, smaller than 10  $\mu\text{m}$ , has recently received much attention from the viewpoint of tertiary oil recovery, emulsion-type liquid membrane treatment, waste water treatment for ships and so on. Conventional separators utilizing the density difference between the oil and drop phases are not effective for emulsions of such small drops. Electrical demulsifying methods are now being actively investigated as a demulsifying technique for emulsions of

very small drops, using an electric pulse of thousands of volts.<sup>1,2,3)</sup> Another type of demulsification technique was also proposed which uses porous membranes and which can be operated under rather mild conditions.<sup>4,5)</sup>

The purpose of this work is to investigate the mechanisms of demulsification using porous membranes.

## 1. Experimental Apparatus and Method

A schematic diagram of the experimental apparatus is shown in Fig. 1. The main part is a stirred tank 6 cm in diameter and 8 cm high. It is fitted with a turbine stirrer with six blades to mix the contents. Details of

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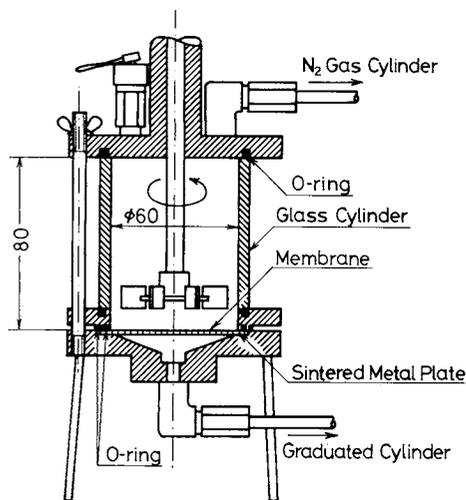


Fig. 1. Main Part of Experimental Apparatus.

the stirrer are shown in Fig. 2. A porous polytetrafluoroethylene (PTFE) membrane is supported on a porous metal plate at the bottom of the tank. The porous metal plate is 2 mm thick and made of stainless steel balls with uniform size of  $70\ \mu\text{m}$ . As the membrane, a porous PTFE membrane with a thickness of  $51\ \mu\text{m}$ , a porosity of 77% and maximum pore size of  $0.67\ \mu\text{m}$  (Gore-Tex 6C5 from Japan Gore-Tex Inc.) was used.  $10^{-4}\ \text{m}^3$  of oil-in-water emulsion was placed in the stirred tank and was pressurized by using nitrogen gas. The stirred tank was set in a water bath and temperature was controlled at  $24\text{--}25^\circ\text{C}$ . In this work, pressure,  $P$ , was kept at  $0.4 \times 10^5\ \text{Pa}$  where only the oil phase, that is, the dispersed phase, was permeated through the membrane.

The permeating velocities of the oil phase,  $N_{\text{oil}}$ , were measured under various conditions. The value of  $N_{\text{oil}}$  was calculated from a curve representing the time dependence of the total amount of oil phase accumulated in a graduated cylinder (Fig. 1). The initial value of  $N_{\text{oil}}$  was derived from the initial slope of this curve. On the other hand, it was revealed that about 1 ml of oil phase was always held in a porous metal plate during each permeation experiment. At the moment when an oil phase was first fed into the graduated cylinder, therefore, 1 ml of oil phase had already permeated through the membrane. All the experimental data were modified by using the 1 ml of oil volume being captured by the porous metal. In each permeation experiment, the initial value of  $N_{\text{oil}}$ , for instance, was taken when the oil volume accumulated in the graduated cylinder reached 3 ml. This means that an emulsion above the membrane at this moment was composed of 50 ml of water phase and 46 ml of oil phase, that is, an emulsion with an oil phase volume fraction of 0.48. Elapsed time,  $t$ , was measured from this moment.

The area of membrane effective for permeation was

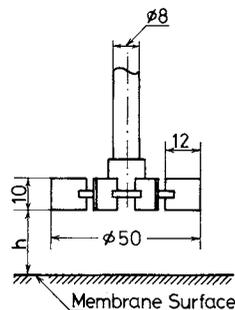


Fig. 2. Details of Stirrer in a Stirred Tank.

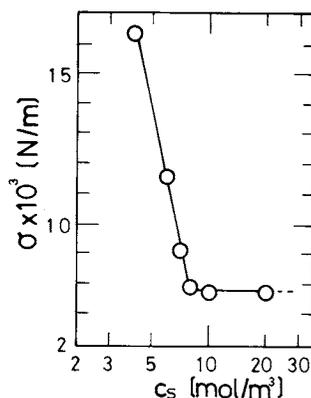


Fig. 3. Interfacial Tension vs. Surfactant Concentration.

$2.83 \times 10^{-3}\ \text{m}^2$ .

## 2. Preparation of Emulsion

Emulsion was made using distilled water and Dispensor, a kind of kerosine supplied by Shell Chemical Co., Ltd. A stirrer-type homogenizer (TERAOKA Emulation B) was used to prepare the emulsion, and  $6 \times 10^{-5}\ \text{m}^3$  of emulsion was obtained each time by stirring  $3 \times 10^{-5}\ \text{m}^3$  each of oil and water phases together for 300–1800 s at a stirring speed of 217 rps. For each permeation experiment,  $10^{-4}\ \text{m}^3$  of emulsion was necessary, and permeation experiments should be carried out several times using the same emulsion (with the same drop size distribution) to determine the effects of operating conditions. On the other hand, it was very difficult to make the same emulsion even if the conditions were carefully controlled. Hence, a sufficient amount of mother emulsion was prepared by mixing emulsions made under the same preparation condition. The emulsion used for each permeation experiment was a part of the mother emulsion thus prepared.

SDS (sodium dodecyl sulfate) was used to stabilize the emulsion. The interfacial tension between oil and aqueous phase was measured by the suspended drop method, and the results are shown in Fig. 3. It is seen that the CMC (critical micelle concentration) of SDS is  $7.6\ \text{mol/m}^3$ . In this work, the concentration of SDS in the aqueous phase,  $c_s$ , was mainly set to be  $2.6\ \text{mol/}$

m<sup>3</sup>. The size range of the emulsion drops was checked by micrographs and was seen to be distributed from 0.5 μm to several μm. The maximum size,  $d_{max}$ , depended on the time length of emulsifying operation,  $t_s$ . The values of  $d_{max}$  are tabulated in **Table 1** referring to  $t_s$ .

### 3. Experimental Results and Discussion

#### 3.1 Effects of drop size

Data of  $N_{oil}$  at  $c_s = 2.6 \text{ mol/m}^3$  for  $d_{max} = 2\text{--}3 \mu\text{m}$ ,  $3\text{--}5 \mu\text{m}$  and  $5\text{--}10 \mu\text{m}$  are shown in **Fig. 4**. The value of oil flux was strongly affected by the drop size. Roughly, it can be said that the value of  $N_{oil}$  becomes ten times larger when  $d_{max}$  is doubled. Oil drops adhering to the PTFE membrane easily permeate through the membrane because a PTFE membrane has little permeation resistance for an oil phase.<sup>4)</sup> Figure 4, therefore, means that larger oil drops can adhere to a PTFE membrane much easier than smaller ones. In other words, larger drops have many more opportunities to touch a surface of the membrane than do smaller ones. This is considered to be an inertial effect.

#### 3.2 Effects of stirring speed

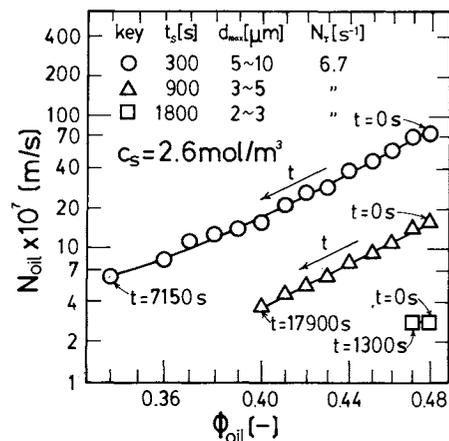
Experimental data of  $N_{oil}$  of emulsion made at  $t_s = 600 \text{ s}$  and  $c_s = 2.6 \text{ mol/m}^3$  are shown in **Fig. 5** for various stirring speeds,  $N_r$ . In each permeation experiment,  $10^{-4} \text{ m}^3$  of emulsion was placed in the stirred tank and the time dependence of  $N_{oil}$  was measured at constant  $N_r$ . In the experiment, the volume fraction of the oil phase,  $\phi_{oil}$ , decreased with time,  $t$ , because only the oil phase was permeating through the membrane. By taking the value of  $N_{oil}$  at  $\phi_{oil} = 0.48$ , the effect of  $N_r$  can directly be investigated as shown in **Fig. 6**. Data for  $t_s = 300 \text{ s}$ ,  $600 \text{ s}$  and  $1200 \text{ s}$  are plotted in **Fig. 6**. The effect of  $N_r$  on  $N_{oil}$  is very large, and the value of  $N_{oil}$  is approximately in proportion to the 4th power of  $N_r$ . Considering that fluid in a stirred tank flows circularly in a vessel, the frequency of drops touching the membrane surface,  $f_r$ , seems to be proportional to  $N_r$  as shown experimentally by Unno *et al.*<sup>5)</sup> However, the exponent 4 is far larger than unity. Some additional factors should exist, such as, for example, the drop velocity approaching the membrane surface, the probability of each drop adhering to the membrane surface at its contact with the surface and so on. The mechanism that explains the effect of stirring speed on the oil flux is not clear at present.

#### 3.3 Effects of distance between stirring blade and membrane surface

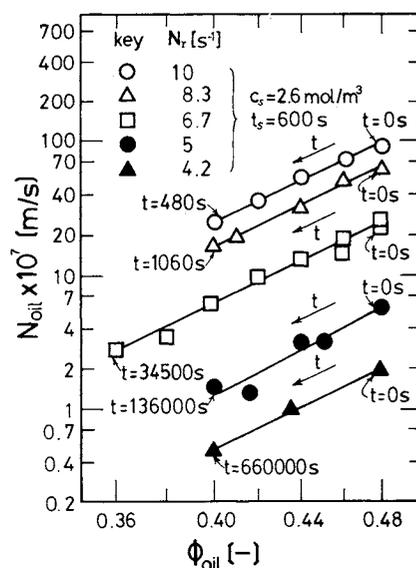
The oil flux data at  $N_r = 6.7 \text{ rps}$  for emulsions made at  $c_s = 2.6 \text{ mol/m}^3$  and  $t_s = 600 \text{ s}$  are shown in **Fig. 7** as a function of the distance between the stirring blades and the membrane surface,  $h$ . As the value of  $h$  decreases from 20 mm to 2.5 mm, the value of  $N_{oil}$

**Table 1.** Relation between  $t_s$  and  $d_{max}$

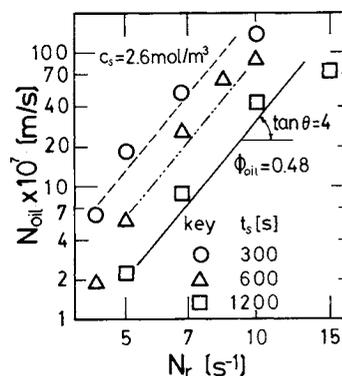
$t_s$ [s]	$d_{max}$ [μm]
300	5~10
600	4~5
1200	3~4
1800	2~3



**Fig. 4.** Effect of Drop Size on Oil Flux.



**Fig. 5.** Oil Flux at Various Stirring Speeds.



**Fig. 6.** Effect of Stirring Speed on Oil Flux.

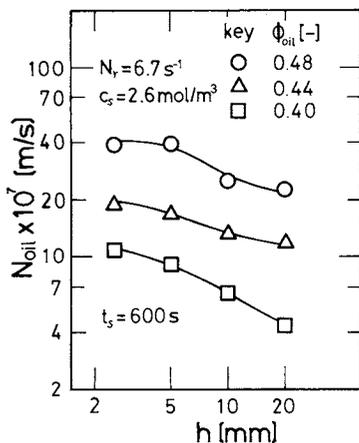


Fig. 7. Effect of Distance between Membrane Surface and Stirring Blades.

increases fourfold or fivefold and approaches the maximum.

### 3.4 Effects of volume fraction of oil phase

A mother emulsion, used as starting material, was prepared by gathering emulsions made under the same preparation conditions, that is,  $c_s = 2.6 \text{ mol/m}^3$  and  $t_s = 600 \text{ s}$ . By using an aqueous solution of SDS having the same concentration as that of the original aqueous phase, the mother emulsion was diluted to emulsions having various values of  $\phi_{oil}$  with the same distribution function of drop size. Emulsions thus prepared were used for permeation experiments to determine the effects of  $\phi_{oil}$ . In Fig. 8, each group of empty plots connected by dotted line corresponds to one batch permeation experiment, and a solid symbol means the initial value in each permeation experiment. The values of  $\phi_{oil}$  and  $N_{oil}$  decrease with time in each permeation experiment, because only the oil phase is permeating through the membrane. The thick solid line represents the initial value behavior of each permeation experiment. Compared with the solid line, each dotted line shows a steeper slope, which means that the value of  $N_{oil}$  decreases with time faster than that expected from the solid line. This is reasonable because larger oil drops permeate through the membrane faster than smaller ones, as seen from Fig. 4. In each permeation experiment in Fig. 8 (each dotted line), the initial value of  $N_{oil}$  almost corresponds to large oil drops and the other values correspond to smaller drops. This is considered to be the reason for the steep slopes of the dotted lines.

To determine the effect of  $\phi_{oil}$  on  $N_{oil}$ , it is preferable to use the same emulsion (having the same drop size distribution). At the initial stage of each permeation experiment in Fig. 8, the drop size distribution was the same as that of the mother emulsion, because each original emulsion was prepared by diluting the same mother emulsion. Hence, the thick solid line can be utilized to see the effect of  $\phi_{oil}$  on  $N_{oil}$ .

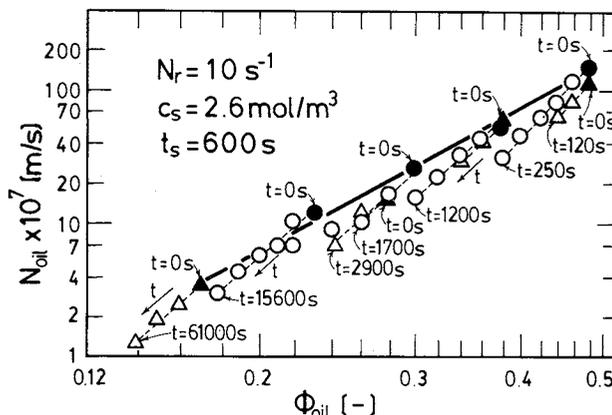


Fig. 8. Effect of Oil Volume Fraction on Oil Flux.

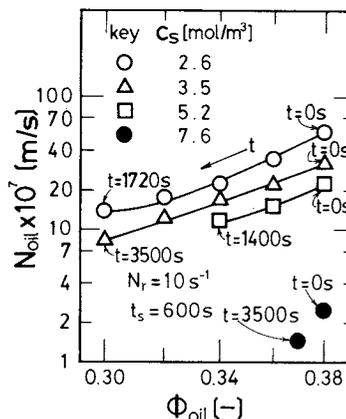


Fig. 9. Oil Flux at Various Surfactant Concentrations.

It can be concluded that the value of  $N_{oil}$  is proportional to the 3.4th power of  $\phi_{oil}$  when  $c_s = 2.6 \text{ mol/m}^3$  and  $t_s = 600 \text{ s}$ . For a different value of  $c_s$  or  $t_s$ , the exponent may become different from 3.4, but it may be expected that the exponent is much larger than unity.

The opportunity of each oil drop to touch the membrane surface is considered to be almost proportional to the value of  $\phi_{oil}$ . This reflects to the expectation that  $N_{oil}$  is proportional to  $\phi_{oil}$ . However, the index number 3.4 is far larger than unity. This means that the mechanism for capturing the oil drops on the membrane surface depends not only on the touching process of each oil drop with the surface, but is also strongly affected by oil drops already present on the membrane surface. Otherwise, such a high value of the index number cannot be understood. However, details of the mechanism are not clear at present.

### 3.5 Effect of surfactant concentration

In Fig. 9, results of permeation experiments are shown using emulsions with various SDS concentrations. In these experiments, mother emulsion was also prepared by gathering emulsions made under the same conditions,  $c_s = 2.6 \text{ mol/m}^3$ ,  $t_s = 600 \text{ s}$  and  $\phi_{oil} =$

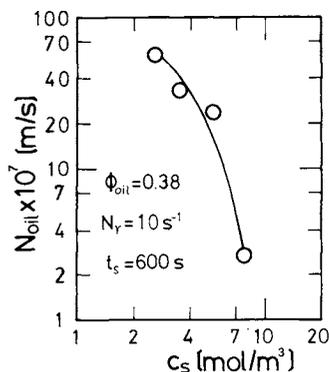


Fig. 10. Effect of Surfactant Concentration on Oil Flux.

0.5. Diluting the mother emulsion to an emulsion of  $\phi_{oil}=0.4$  with an appropriate SDS aqueous solution, the emulsion for each permeation experiment was prepared. Hence, the size distribution of oil drops is identical in all permeation experiments. The value of  $N_{oil}$  decreases when the value of  $c_s$  increases. The values of  $N_{oil}$  at  $\phi_{oil}=0.38$  for various values of  $c_s$  are plotted in Fig. 10. When  $c_s$  is increased to the CMC, that is,  $7.6 \text{ mol/m}^3$ , the value of  $N_{oil}$  becomes very small. The higher the surface concentration of SDS, the smaller becomes the permeation flux of oil phase. It can be deduced from these results that SDS molecules adsorbed on the surface of oil drops are aligned with the outwardly directed hydrophilic groups, and prohibit the oil drops from adhering to the PTFE membrane. This effect seems to become stronger when the surfactant molecules are more tightly aligned on a drop surface. If the surfactant molecules are loosely distributed on a drop surface, a free surface area or a surface area with very low surfactant concentration can be formed on the drop surface, and the oil drop can easily adhere to the PTFE membrane through the surface area.

### Conclusions

Oil-in-water emulsions were permeated through the porous PTFE membrane, and factors influencing the oil permeation velocity were experimentally investigated. The following results were obtained, keeping the pressure constant at  $0.4 \times 10^5 \text{ Pa}$  and the surfactant (SDS) concentration at  $2.6 \text{ mol/m}^3$  where only the oil phase was permeated through the membrane.

1. When the maximum size of the oil drops is doubled, the value of the oil flux becomes almost ten times larger.

2. The value of the oil flux is proportional to the 4th power of the stirring speed.

3. The value of the oil flux increases fourfold or fivefold when the distance between the stirring blade and the membrane surface is decreased from 20 mm to 2.5 mm.

4. The value of the oil flux is proportional to 3.4th power of the volume fraction of oil phase when  $c_s = 2.6 \text{ mol/m}^3$  and  $t_s = 600 \text{ s}$ .

When the surfactant concentration is changed, it was revealed that the oil flux decreases to a very small value as the surfactant concentration increases up to the critical micelle concentration.

### Acknowledgment

The authors are grateful to Japan Gore-Tex Inc. for supplying Gore-Tex membranes.

### Nomenclature

$c_s$	= concentration of sodium dodecyl sulphate in aqueous phase used to make emulsion	[mol/m <sup>3</sup> ]
$d_{max}$	= maximum size of drops	[ $\mu\text{m}$ ]
$h$	= distance between stirring blades and a membrane surface	[mm]
$N_r$	= rotating speed of a stirring blade during permeating operation	[s <sup>-1</sup> ]
$N_{oil}$	= permeating flux of oil	[m/s]
$P$	= static pressure	[Pa]
$t$	= elapsed time	[s]
$t_s$	= time length of emulsifying operation	[s]
$\sigma$	= interfacial tension between oil and water phases	[N/m]
$\phi_{oil}$	= volume fraction of oil phase	[—]

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