

OIL SEPARATION FROM OIL-WATER MIXTURE BY A POROUS POLY(TETRAFLUOROETHYLENE) (PTFE) MEMBRANE

HAIJIME UNNO, HISAO SAKA AND TAKASHI AKEHATA

*Department of Environmental Chemistry and Engineering,
Tokyo Institute of Technology, Yokohama 227*

Key Words: Membrane Separation, Porous Teflon Membrane, Oil-Water Separation, Emulsion, Demulsification

Factors affecting oil separation from surfactant-free dispersed oil-water mixture in a mixing tank by a poly(tetrafluoroethylene) (PTFE) membrane separator unit were investigated. The typical unit consisted of a sheet of porous PTFE membrane, a PTFE filter paper and an acrylic perforated plate. The separation process included three steps in series: 1) attachment of dispersed oil droplets to the membrane surface, 2) penetration of the attached oil into and through the porous space within the membrane and the filter paper, and 3) release of the oil from the separation unit. The resistance of step 2) was negligibly small compared with the other two steps. The ratio, α , of the oil droplet amount separated by the separation unit to that colliding with the membrane surface was very small, i.e., 3% at most within the experimental conditions. The effect of oil viscosity was significant and the ratio α was inversely proportional to the oil viscosity.

Introduction

Application of poly(tetrafluoroethylene) (PTFE) membrane to the separation of oil from oil-water mixture has attracted much interest recently in connection with oily wastewater treatment, demulsification⁵⁾ in liquid film separation processes, extraction in the field of analytical chemistry,⁴⁾ etc.

Because of the highly hydrophobic nature of PTFE, porous membranes of PTFE are promising for application to oil-water separation. However, fundamental knowledge about the separation mechanism is scarce. This paper concerns an experimental analysis of factors affecting oil separation from a surfactant-free oil in water emulsion in a mixing tank through a porous PTFE membrane. The rate-determining step of the oil-water separation is discussed.

1. Experimental Apparatus and Procedure

The apparatus is shown in Fig. 1. It consisted of an acrylic tank ② fitted with a PTFE membrane separator unit ① and a water bath ③. The acrylic tank, 14.4 cm in diameter and 21.5 cm in height, was fitted with four acrylic baffle plates ④ of 1.5 cm width, a stainless steel screw-type impeller ⑤ with three blades of 5.0 cm diameter and 45° pitch, and an acrylic inner tube ⑥ of 7.1 cm diameter. The inner tube was set at a height h of 2.0 cm from the bottom, as shown in the figure. The height h of 2.0 cm was confirmed to be the

most efficient for oil-water separation by this experimental configuration.

The PTFE membrane separator unit ① was installed at the center of the tank bottom as shown in Fig. 1. The PTFE membrane ⑦ to be tested, obtained from Furon Kogyo Co., was mounted on a sheet of PTFE filter paper ⑧, obtained from Nissan Riko Co. The filter paper was supported by a perforated acrylic plate ⑨. The filter paper was so coarse that the flow resistance of oil was negligibly small compared with

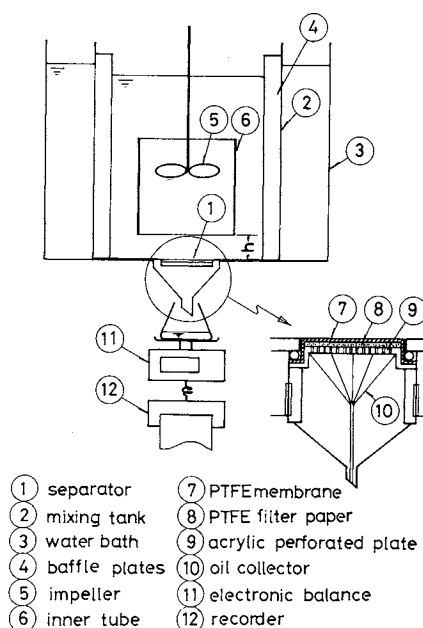


Fig. 1. Experimental apparatus.

Received November 18, 1985. Correspondence concerning this article should be addressed to H. Unno. H. Saka is now with Tokyo Gas Co.

that of the PTFE membrane. The effective area of the PTFE membrane was circular and its diameter was 4 cm. Two different types of membrane, i.e., porous and stretched, were used. The membrane surface structure is shown as SEM images in Fig. 2. The properties of the PTFE membrane used are summarized in Table 1.

The oil and water used were kerosene and distilled water, respectively. The temperature range was from 290.5 to 332.5 K.

A 2.295 dm³ quantity of distilled water in the tank was stirred beforehand at an impeller speed *N*. The water in the inner tube ⑥ was propelled by the impeller ⑤ to the membrane region at the tank bottom. After the steady state of liquid flow in the tank was attained, 115 cm³ of kerosene was poured instantaneously onto the water surface. Immediately after the addition of oil to the water the oil was disintegrated into droplets by the fluid flow or directly by the impeller. The drops formed were transported to the tank bottom by the bulk liquid flow, and the oil started to pass through the membrane. The oil separated was collected by a collector ⑩, the collected oil being weighed and recorded continuously by an electronic balance ⑪ and a recorder ⑫, respectively.

The impeller's rotational speed was from 13.3 to 16.7 s⁻¹, which was sufficiently high to maintain a homogeneous dispersion of oil but sufficiently low to ensure no air entrainment.

The fluid flux to the membrane surface was measured by the electrolytic particle tracer method (EPTM).³⁾ The method is outlined in the Appendix.

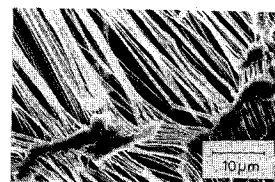
2. Experimental Results and Discussion

The size of the droplet in the mixing tank was observed microscopically during the separation experiment and its distribution range was fairly wide, i.e., from 150 down to 10 μm or less. The droplets were circulating with the water flow through the inner tube. Some of the droplets were conveyed to the membrane surface, to which the droplets attached. Some portion of the attached oil penetrated the membrane and finally flowed out of the unit, but the rest was detached from the membrane surface, returning into the bulk flow in the mixing tank.

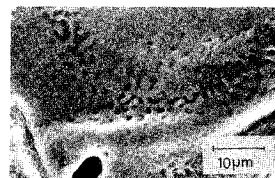
2.1 General remarks on oil separation

Figure 3 shows some examples of the recorded amount of separated oil *W(t)*. From Fig. 3, some residual oil that had not separated from the water within the experimental time period was observed. It seems that the residual oil amount became greater when a membrane of smaller pore size was used.

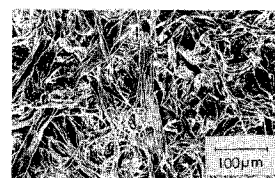
Figures 4 and 5 show calculated relationships between the oil separation rate *Q(t)* defined by Eq. (1) and the residual oil concentration *C(t)* in the mixing tank, the parameters being the nominal pore size of



stretched PTFE membrane (*d* = 1 μm)



porous PTFE membrane (*d* = 10 μm)



PTFE filter paper

Fig. 2. Scanning electron microscopy images of PTFE membranes and filter paper.

Table 1. Properties of membrane

Structure	PTFE membrane				PTFE filter paper
	Stretched		Porous		
Nominal diameter d [μm]	1	2	5	10	—
Thickness [μm]	100	105	100	145	550
Porosity [—]	0.81	0.81	0.67	0.60	0.75
Density [g/cm ³]	0.41	0.41	0.71	0.88	—

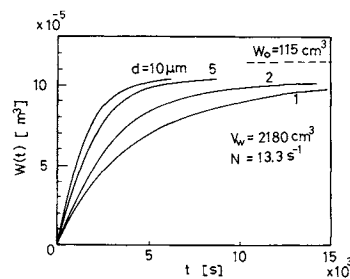


Fig. 3. Example of separated oil amount *W(t)*.

the PTFE membrane, *d*, and the impeller speed, *N*, respectively.

$$Q(t) = \frac{W(t_2) - W(t_1)}{A \cdot (t_2 - t_1)} \quad (1)$$

$$t = \frac{t_1 + t_2}{2}$$

$$C(t) = \frac{W_0 - W(t)}{V_w + (W_0 - W(t))} \quad (2)$$

where *V_w* and *W₀* are respectively the oil and the

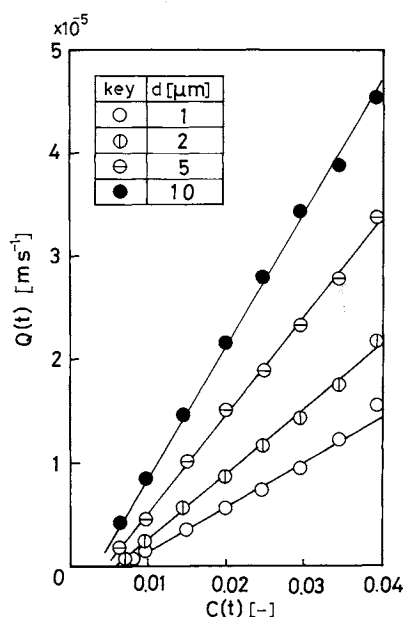


Fig. 4. Examples of relation between oil separation rate $Q(t)$ and residual oil concentration $C(t)$ ($N=13.3 \text{ s}^{-1}$).

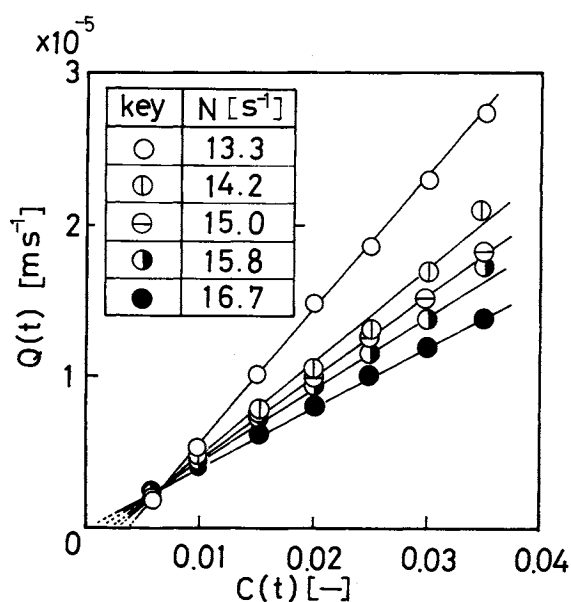


Fig. 5. Examples of relation between oil separation rate $Q(t)$ and residual oil concentration $C(t)$ ($d=5 \mu\text{m}$).

water volume charged initially.

The separation rate $Q(t)$ showed a linear dependence on the residual oil concentration $C(t)$ independently of the type of separation membrane used, though the separation rates varied with nominal pore size of the membrane.

The limiting residual oil concentration C_∞ , which was given by the extrapolated intercept of the experimental data and the residual concentration axis $C(t)$, decreased with increasing impeller speed. It seems that the limiting residual concentration C_∞ approached zero as impeller speed increased

sufficiently.

Oil droplets of smaller size were considered to be difficult to contact with the membrane surface because of their smaller momentum. Therefore, the residual oil can be explained qualitatively by the wide size distribution with much smaller droplets. As time elapsed the oil concentration in the mixing tank became smaller, due to the separation of the larger droplets. The small droplets were hardly coalesced to form larger droplets, and this fact resulted in residual oil. Since the momentum of an oil droplet, even one of small size, increased with impeller speed, the smaller oil droplet was considered to have had a higher chance to attach to the membrane surface. Therefore, the limiting residual oil concentration decreased with increasing impeller speed as shown in Fig. 5. However, since all the related factors have not yet been evaluated, a quantitative analysis of the apparent dependence of residual oil amount on membrane pore size and impeller speed was left to further study.

2.2 Separation rate of oil

From Figs. 4 and 5 the oil separation rate $Q(t)$ is expressed by Eq. (3).

$$Q(t) = B \cdot (C(t) - C_\infty) \quad (3)$$

where $C(t) - C_\infty$ and B are respectively a concentration difference that decreased to zero at sufficiently long time of operation and a separation rate coefficient. The coefficient B is given by the slope of Figs. 4 and 5, and depended on the oil separation resistance.

Figure 6 shows the relationship between the separation rate coefficient B and the impeller speed N . The coefficient B decreased with increasing impeller speed N . The oil separation took place as already described, by three processes in series: i) attachment of oil droplet to the PTFE membrane surface from the bulk emulsion, ii) oil penetration through the membrane of the separation unit, and iii) release of the oil mass from the unit to the oil collector. Therefore, the oil separation is modelled as shown in Fig. 7. To analyze the factors affecting the separation rate coefficient B shown in Fig. 6, it is necessary to clarify the contribution of the three processes to the separation rate.

Figure 8 shows an example of the effect of the membrane layer arrangement of the separation unit on the separation rate $Q(t)$. Arrangements #1 through #3 showed no remarkable difference in the separation rate $Q(t)$, and therefore coefficient B was constant. Since the conditions for the upper and lower surfaces of the separator unit, i.e., the oil-water mixture side and the oil collection side of the unit respectively, were identical for all the separation experiments, it may be concluded that the oil flow resistance in the membrane matrix was negligibly small compared with

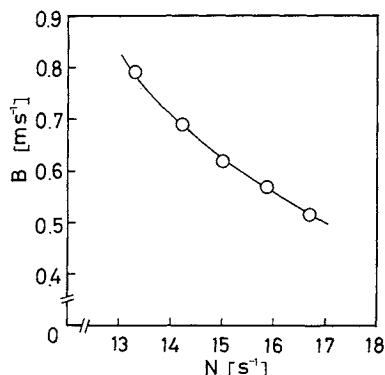


Fig. 6. Relation between separation rate coefficient B and impeller speed N ($d = 5 \mu\text{m}$).

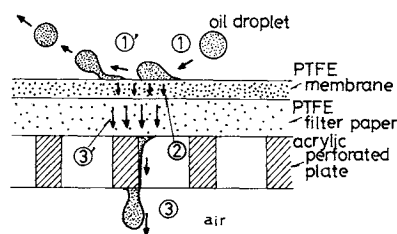


Fig. 7. Model of oil separation from oil-water mixture: ① oil drop approaches PTFE membrane; ①' oil drop detaches from PTFE membrane; ② oil attached to membrane penetrates through pore of membrane; ③ oil releases from PTFE filter paper; ③' oil flows through PTFE filter paper.

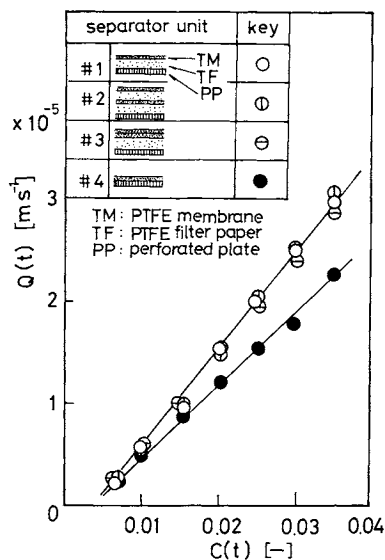


Fig. 8. Effect of membrane arrangement on oil separation ($d = 5 \mu\text{m}$).

those of the other two processes, i) and iii), listed above.

By comparing the results of #1 and #4 of Fig. 8, the effect of the condition for the oil collection side of the separator unit was observed. The membrane of unit #1 was supported by a sheet of PTFE filter paper which was supported by the perforated plate, while the membrane of unit #4 was supported directly by

the perforated plate. Since the pore spaces of both PTFE membrane and filter paper were filled with penetrated oil, the above results imply that there was some difference in two interactions—1) that among the PTFE filter paper, the acrylic perforated plate, oil and air, and 2) that among the PTFE membrane, the acrylic perforated plate, oil and air. PTFE is a highly hydrophobic material but still oilphobic since the critical surface tension²⁾ of PTFE is $18 \times 10^{-3} \text{ N/m}$ and the surface tension of kerosene is $31 \times 10^{-3} \text{ N/m}$. Therefore, the interaction among the oil, air and PTFE membrane of PTFE filter paper would have been significant among the other interactions. A quantitative analysis of this point remains to be made in future.

As described already, there might exist some oil droplets which did not pass through the membrane even though they had reached the surface. Therefore, it is necessary to consider the efficiency of oil separation. This can be done by evaluating the ratio, α , of oil mass separated by the separator unit to that reached the membrane surface. In other words, the ratio α represents the probability that an oil droplet reaching the membrane surface is separated by the unit. When the liquid flux to the membrane, i.e., the oil-water mixture conveyed to the membrane surface by the impeller per unit time, is represented by Φ , $\Phi \cdot (C(t) - C_\infty)$ represents the effective oil flux to the membrane. Therefore, from Eq. (3) the separation probability α is defined by Eq. (4).

$$B = \alpha \cdot \Phi \quad (4)$$

The flux Φ was measured by the electrolytic particle tracer method (EPTM)³⁾ as described in Appendix.

Figures 9 and 10 show the relationship between the flux Φ and the impeller speed N , and that between the passage probability α and the impeller speed N , respectively. From Fig. 9 the fluid flux Φ was proportional to the impeller speed N as

$$\Phi = 1.25 N \quad (5)$$

From Fig. 10 it is shown that the separation probability α was very low.

From Figs. 5, 9 and 10 it is concluded that though the fluid flux increased linearly with increasing impeller speed, the separation probability α decreased with increasing N , and the decrease of α resulted in the decrease of the separation coefficient B . The separation probability was considered to be dependent on the oil droplet attachment process ① and the detachment process ①' shown in Fig. 7. These two steps were affected by the fluid flow near the membrane surface, which was represented by the flux Φ .

The decrease of B with increasing N is due to the fact that the increasing rate of detachment process ①' was greater than that of attachment process ①. The

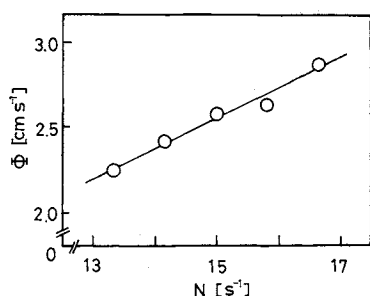


Fig. 9. Relationship between fluid flux to membrane Φ and impeller speed N .

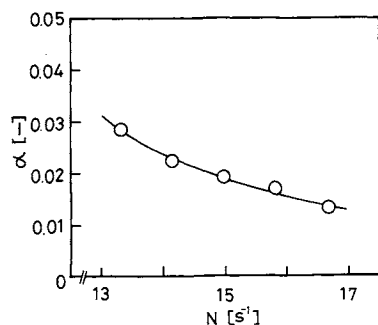


Fig. 10. Relation between separation probability α and impeller speed ($d = 5 \mu\text{m}$).

magnitude of the rate difference in processes ① and ①' was related intimately to the oil separation process. However, the above discussion does not show that the process i), represented by steps ① and ①' in Fig. 7, was the sole rate-determining process.

Figure 11 shows an example of the effect of temperature on the separation. The effect of temperature on the physical properties of the oil and water was mainly on viscosity. The changes in the density and surface tension of kerosene and water are negligibly small. From the above consideration a relationship between the separation probability α and the viscosity was obtained as shown in Fig. 12. The separation probability α was inversely proportional to the oil viscosity. This implies that there existed an effect of oil flow on the separation. Processes ① and ①' would have been affected also by the oil viscosity. The process of oil release from the membrane to the collector may have been affected by the viscosity as well.

Conclusion

Factors affecting the separation of oil from oil-water mixture in a mixing tank by a poly(tetrafluoroethylene) membrane were studied. The separation process consisted of three steps: attachment of oil droplets to the membrane surface, penetration of the attached oil through the separation unit, and oil release from the unit to the oil collector. The results are summarized as follows:

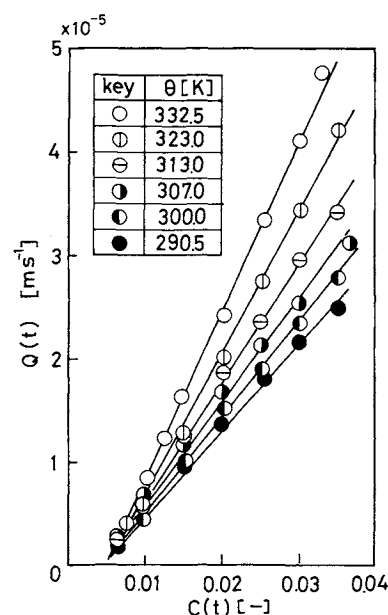


Fig. 11. Effect of temperature on oil separation rate.

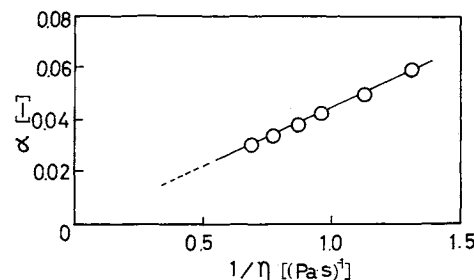


Fig. 12. Correlation between separation probability α and viscosity η .

1) The flow resistance within the membrane was negligibly small compared with those of the oil-water mixture side of the membrane and the release of the permeated oil from the separation unit.

2) The separation probability of oil droplets, reaching the membrane surface, was very low, i.e., 3% at most within the experimental conditions.

3) The effect of the membrane arrangement of the separator was significant.

4) The effect of the oil viscosity on the separation was significant.

Appendix

A detailed description of the electrolytic particle tracer method (EPTM) has appeared elsewhere.³⁾ Specific points of the present experiment were as follows:

1) Copper working electrode of 40 mm diameter, which was the same size as the separation membrane, was installed at the place where the membrane was set.

2) Counter electrode of copper, of 80 × 30 mm rectangular shape, was installed near the liquid surface.

3) Reference electrode was a calomel electrode.

4) The liquid in the tank was an electrolyte solution of $3 \times 10^{-3} \text{ mol/dm}^3 \text{ KH}_2\text{PO}_4$ and $3 \times 10^{-3} \text{ mol/dm}^3 \text{ K}_2\text{HPO}_4$.

5) The tracer particle was a polystyrene particle covered with

aluminum foil, and the particle density was adjusted to that of the solution.

The fluid flux Φ was calculated from the frequency F of tracer particle collision with the working electrode, i.e., the membrane area based on the following reasoning. The motion of a fluid element colliding with the membrane area can be replaced conceptually by a picture in which the fluid element flows out of the tank through the membrane area at the instant of the collision, and at the same instant the element flows back into the tank again. Therefore, if the movement of the tracer particle is the same as that of the fluid element, the time interval between the two consecutive collisions represents the residence time of the fluid element in the conceptual continuous flow through the tank with a flow rate $q = A \cdot \Phi$. Since this conceptual flow system is a closed system,¹⁾ the flow rate is calculated by Eq. (A1).

$$q = V/T \quad (\text{A1})$$

where V and T are respectively the liquid volume in the tank and the mean residence time given by a reciprocal of the mean collision frequency, which is calculated by the measured collision number divided by the time of the measurement. Therefore, the fluid flux is calculated by Eq. (A2).

$$\Phi = q/A \quad (\text{A2})$$

Nomenclature

A	= membrane surface area	[m ²]
B	= separation rate coefficient	[m/s]

$C(t)$	= residual concentration of oil	[—]
C_{∞}	= limiting residual concentration of oil	[—]
d	= nominal pore size of PTFE membrane	[μm]
F	= collision frequency of tracer particle	[s ⁻¹]
$Q(t)$	= separation rate	[m ³ /s]
q	= imaginary liquid flow rate	[m ³ /s]
T	= mean residence time	[s]
t	= time	[s]
V	= liquid volume in the tank	[m ³]
V_w	= water amount charged initially	[m ³]
$W(t)$	= oil amount separated till time t	[m ³]
W_o	= oil amount charged initially	[m ³]
t_1, t_2	= time for measurement	[s]
α	= separation probability	[—]
Θ	= temperature	[K]
Φ	= fluid flux to the membrane	[m/s]

Literature Cited

- 1) Danckwerts, P. V.: *Chem. Eng. Sci.*, **2**, 1 (1953).
- 2) Hamilton, W. C.: *J. Colloid & Interface Sci.*, **40**, 219 (1972).
- 3) Sakai, Y., H. Unno and T. Akehata: *J. Chem. Eng. Japan*, **18**, 564 (1985).
- 4) Tamura, S.: *Kagaku-Zoukan*, p. 177 (1978).
- 5) Ueyama, K., S. Kittaka and S. Furusaki: *Kagaku Kogaku Ronbunshu*, **10**, 775 (1984).