Emulsion Breakdown: Mechanisms and Development of Multilayer Membrane

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Phase inversion phenomena of oil-in-water (triolein in water-containing sodium lauryl sulfate, SDS) emulsions permeating through hydrophobic micropores were visualized using an optically accessible array of well-defined microchannels and a microscope video system. Oil droplets coalesced on the hydrophobic microchannel surface and permeated to form a continuous oil layer at the outlet. Water was repelled from the surface, and large, irregular-sized water droplets were created at the outlet. To evaluate the emulsion breakdown mechanism practically, the emulsions were filtered with hydrophobic polytetrafluoroethylene membranes of several pore sizes. In all cases, the permeate was separated into two phases, an oily and an aqueous one. The three pore sizes, 1-, 5- and 10-μm membranes, were stacked into a layer, and with the multilayer membrane the breakdown ability of the 1-μm membrane was effectively combined with the oil droplet growth ability of the 5- and 10-μm membranes.

Introduction

Membrane treatment for oil-in-water (O/W) emulsions has been studied for several years. Most of the studies aimed at a concentration of the dispersed oily phase in the retentate side and removal of the continuous phase to the permeate side through the membrane pores. For this strategy, a hydrophilic membrane should be used for the O/W emulsion to prevent fouling by oil droplets. Several types of membranes have been applied: ceramic microfiltration membranes (Schwering et al., 1993; Lahiere and Goodboy, 1993; Murase et al., 1996), glass microfiltration membranes (Nakashima and Shimizu, 1989, 1994), ceramic and organic microfiltration membranes (Koltuniewicz et al., 1995), and ultrafiltration membranes (Lee et al., 1984; Belkacem et al., 1995; López, 1995). As a variation, a water-in-oil-in-water (W/O/W) emulsion was filtered with ultrafiltration membranes (Juang and Jiang, 1994), while a water-in-oil (W/O) emulsion was separated with hydrophobic hollow-fiber membranes (Tirmizi et al., 1996). Farnand et al. (1985) examined several organic membranes for dewatering O/W (bitumen/water) emulsion and reported that two-phase permeation was observed with the use of a hydrophobic PTFE membrane. The phase separation of the permeate occurred by coalescence of oil droplets on the hydrophobic membrane surface. Kawashima et al. (1991) reported phase inversion of W/O/W emulsions to W/O emulsions using polycarbonate membranes. This emulsion breakdown capability was positively applied using a membrane that has attractive interaction with the dispersed phase of an emulsion: hydrophobic membranes for O/W emulsions (Unno et al., 1986; Ueyama et al., 1987; Daiminger et al., 1995; Hlavacek, 1995) and hydrophilic membranes for W/O emulsions (Keurentjes et al., 1991).

Kikuchi et al. (1992, 1994) developed a microscope video system and optically accessible microchannels formed in a single-crystal silicon plate. This microscope video system was used for diagnosing blood-cell deformability by observing permeability through the silicon microchannel. Kawakatsu et

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al. (1996) proposed a novel visualization method for microfiltration phenomena using the same microscope video system and the silicon microchannel where the array of microchannels effectively forms a hydrophilic microfiltration membrane. They observed the filtration phenomena through the microchannel array using O/W and W/O emulsions as feed suspensions. Oil droplets in an O/W emulsion behaved as solid particles at a low transmembrane pressure and permeated through the microchannel array with deformation at a higher pressure. In contrast, water droplets in a W/O emulsion coalesce on the microchannel surface, and large oil drops were produced at the permeate side.

In this article, visualization of the phase-inversion phenomena of O/W emulsions is presented using the microscope video system and a microchannel plate, modified with a hydrophobic silane coupler reagent. Additionally, the O/W emulsion was filtered with PTFE membranes of several pore sizes at several operating pressures to investigate the utilization of the emulsion breakdown mechanism. Different pore-size membranes were multilayered to obtain a novel technique to effectively break down the emulsion.

Materials and Methods

Chemicals

High oleic sunflower oil (triolein, $>90\%$ purity) was obtained from Nippon Lever B.V. (Tokyo, Japan). Sodium lauryl sulfate (SDS, HLB: 40) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The silane coupler reagent, octyltriethoxysilane, LS-5580 was obtained from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan) and applied for the surface modification of the silicon microchannel.

Preparation of O/W emulsification

The 10 liters of water containing 0.5-kg triolein and 0.01 (or 0.03)-kg SDS was homogenized for two hours at 25°C using a batch-scale homogenizer purchased from Nihon Seiki Kaisha, Ltd.

Silicon microchannel plate

Figure 1 illustrates the microchannel plate and the feed flow. The silicon microchannel plate measures 15 mm$\times$15 mm. The thickness of the plate is 0.5 mm. A hole of 1.5 mm $\times$1.5 mm is made at the center of the plate. The actual shape of the microchannel cross section is not rectangular but trapeziform, because of the wet etching characteristics in photolithography processes. The bottom channel width, top channel width, channel wall height, and the equivalent channel diameter are 1.3 μm, 8.7 μm, 4.6 μm, and 4.2 μm, respectively. The distance from a microchannel to a neighbor is 15 μm; 2,600 (650 for one side, $\times$4) microchannels are created in the microchannel plate. The flat area (called terrace) is created at the entrance and the exit of the microchannel array. In order to make a stable hydrophobic microchannel plate and a bottom glass plate, a silane coupler reagent, octyltriethoxysilane, was applied to both for surface modification. The microchannel plate and glass plate were washed with 0.1 M nitric acid for 30 min and with pure water for 30 min. After drying at 80°C, they were dipped in 5 wt. % octyltriethoxysilane solution in toluene and heat treated at 110°C for 1 h (temperature gradient was 1°C/min). Finally, the membranes were ultransonicated several times in toluene to rinse out the unreacted materials.

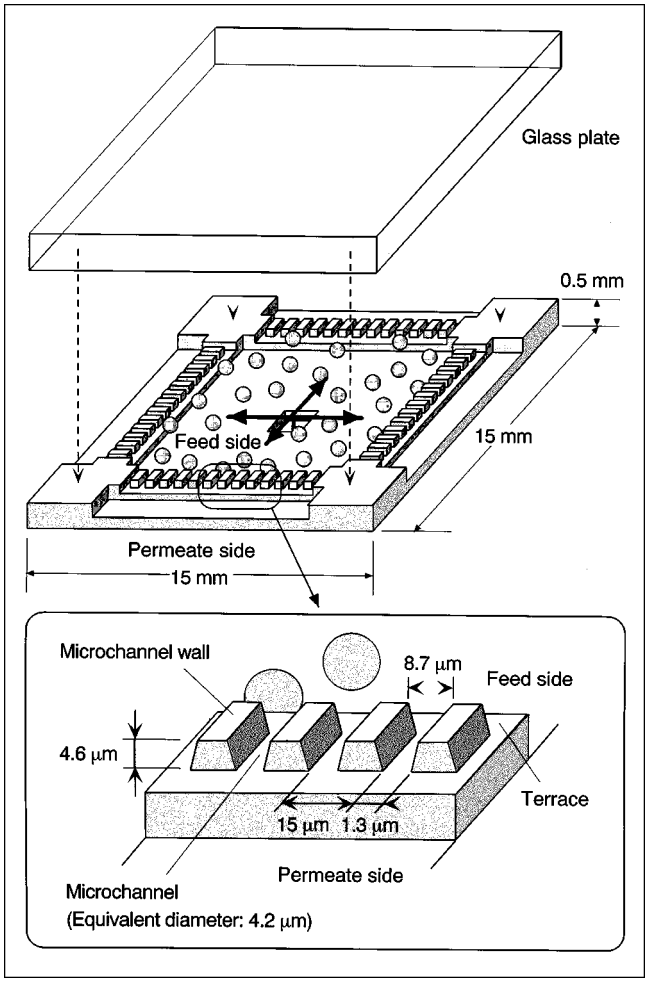

Figure 1. Microchannel plate and feed flow.

Microscope video system

Figure 2 shows the experimental apparatus for visualization of O/W emulsion permeating through the hydrophobic microchannels. The silicon microchannel plate was tightly pressed onto a flat glass plate. The O/W emulsion was supplied into a space between the microchannel plate and the glass plate from the back side of the microchannel plate through its center hole. The operating pressure and the flow rate were regulated by changing the height of the chamber filled with the feed emulsion. An inverted metallographic microscope (TS-V, Chuo Precision Industrial Co., Ltd., Japan) was used to observe images around the microchannels, which were recorded by an 8-mm video camera (CCD-TR900, SONY corporation, Japan). Optical magnification of the objective lens and eyepiece were both 10$\times$. The zoom lens of the video camera (usually applied at a focal length of 62.4 mm) gave additional magnification. Therefore, the final magnification was about 1,000$\times$.

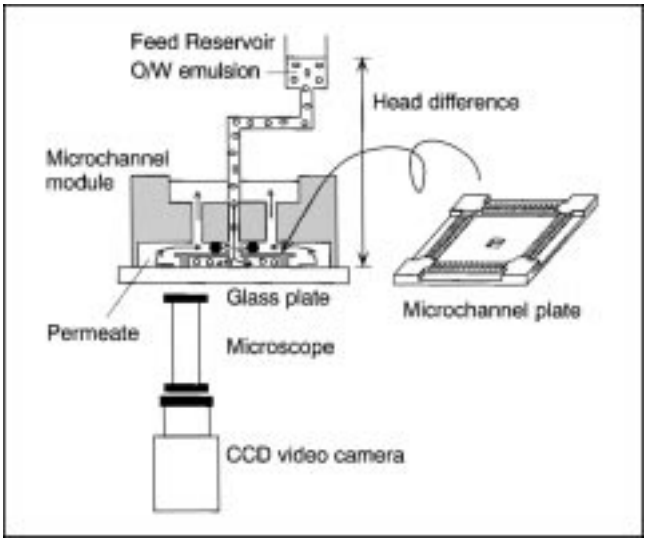

Figure 2. Experimental apparatus for visualization of O/W emulsion permeating through the hydrophobic microchannels.

Membranes and filtration apparatus

Hydrophobic PTFE membranes, types LCWP (nominal pore size: 10 μm), LSWP (5 μm), and FAWP (1 μm) were purchased from Nihon Millipore, Ltd. For microfiltration experiments, a dead-end batch cell, C-70B (Nitto Denko Co.) of 0.0035-m^2 exposed membrane area was used at 25°C. Before being placed in the cell, the membrane was wetted by alcohol, which was then replaced by deionized water. However, in a number of cases, dewetting of the membrane took place during assembly of the filtration cell. The operating pressure was applied by nitrogen gas. The permeate was separated into two phases, an oily one (top fraction) and an aqueous one (bottom fraction). The first 0.06 ($\pm$0.01) kg of the permeate was collected, and each fraction was freeze-dried to measure the oil weight including SDS as an oily residue.

Results and Discussion

Visualization of phase inversion

Figure 3 shows images of an O/W (triolein/water containing 0.1 wt. % SDS) emulsion permeating through hydrophobic microchannels at 8.8-kPa transmembrane pressure (head difference: 0.9 m). The droplet size of the feed emulsion was roughly over the range of 1–10 μm (Figure 3a). Oil droplets coalesced on the terrace at the entrance of the microchannel because of attractive interaction between the oil droplets and the hydrophobic surface. An oil layer was built up on the terrace at the exit of the microchannel array (O). The continuous phase in the feed water was repelled from the terrace and microchannel surface and squeezed through the microchannels (W). The images from Figure 3c to 3j were con-

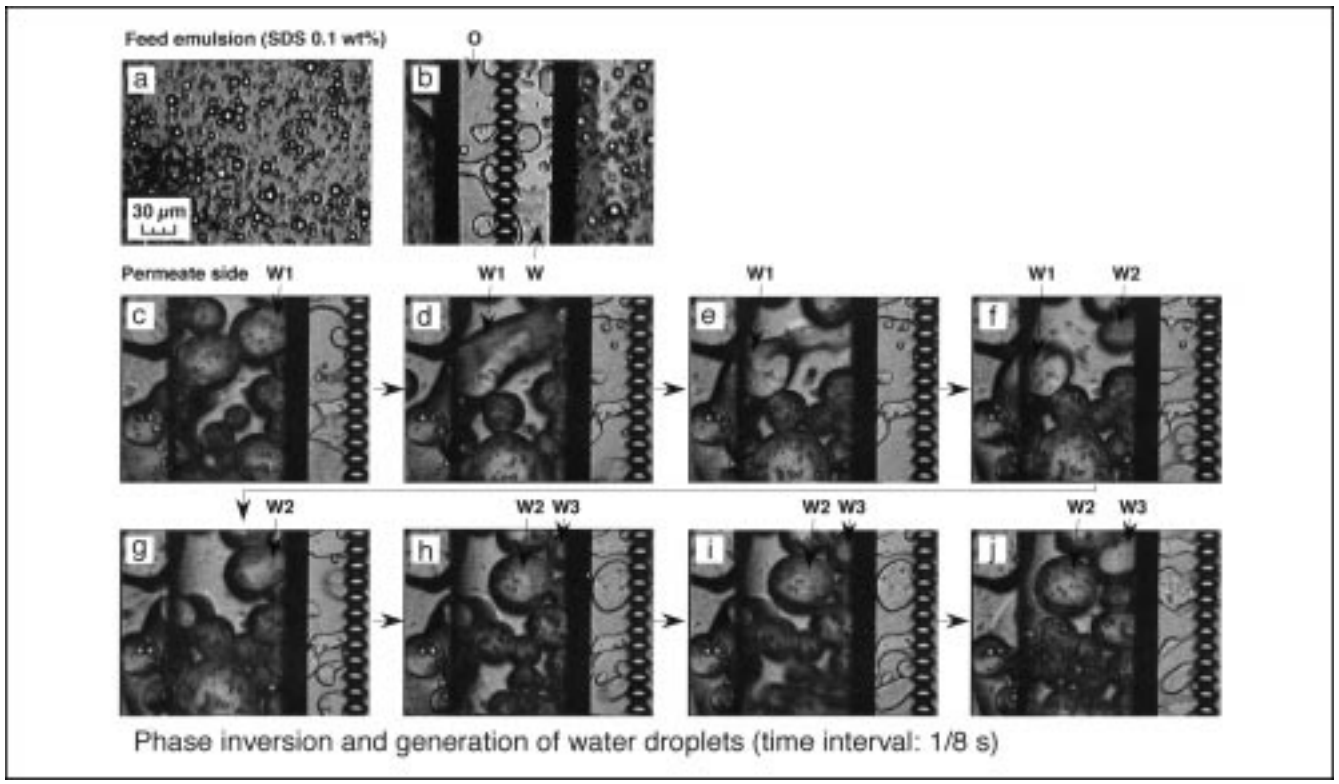

Figure 3. O/W (triolein/water containing 0.1 wt. % SDS) emulsion permeating through hydrophobic microchannels at 8.8 kPa (head difference: 0.9 m).

W, W1, W2, and W3 denote water; O denotes oil (triolein).

tinuously captured every 1/8 s. The accumulated oil moved gradually toward the permeate side and formed a continuous oil layer. In contrast, water intermittently spilled through the oil layer into irregular-sized droplets (e.g., W1, W2, and W3). It was concluded that the O/W emulsion was phase inverted by the permeation through the hydrophobic microchannel, through the generation of irregular W/O droplets. A magnified image around the microchannels is shown in Figure 4. Large oil droplets were adsorbed on the terrace surface before reaching the microchannels. Small droplets were adsorbed and coalesced at the inlet of the microchannels and partially adsorbed on the microchannel wall. An oil layer was formed and remained in a flat space, terrace at the outlet of the microchannels. Water passed through one of the microchannels and water droplets were temporarily generated.

Figure 5 shows images of O/W emulsion containing 0.3 wt. % SDS. The droplet size was 1–5 μm, smaller than that with 0.1 wt. % SDS. The oil droplets partially coalesced during permeation (e.g., O), but most of them accumulated in front of the microchannel array. A cluster of oil droplets sometimes broke through the microchannel and were dispersed at the permeate side (e.g., C). The oil droplets with 0.3 wt. % SDS were more stable than those with 0.1 wt. % SDS because the critical micelle concentration (CMC) of SDS is 0.20–0.23 wt. % (Igarashi, 1991). Beyond CMC, the number of free SDS molecules is saturated and an excess amount of SDS molecules necessary to maintain oil–water interfaces is supplied from SDS micelles like the storage of free molecules.

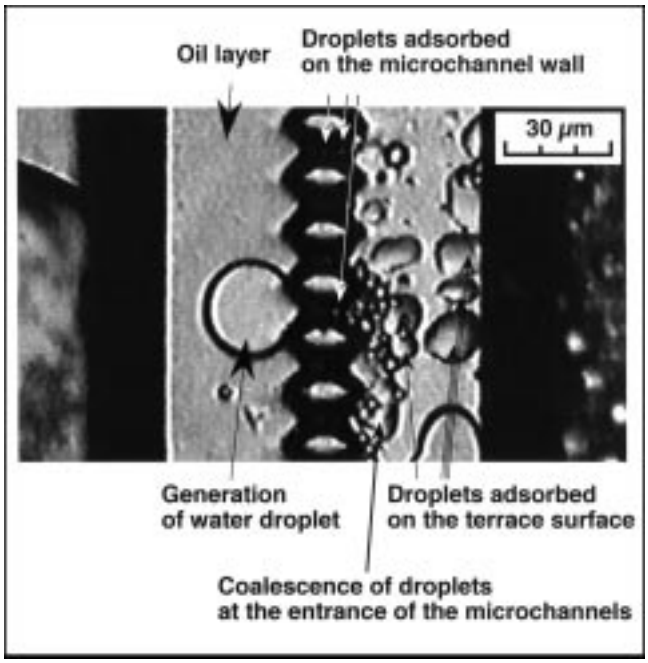

Figure 4. Magnified image around microchannels in demulsification of O/W (triolein/water containing 0.1 wt. % SDS) emulsion.

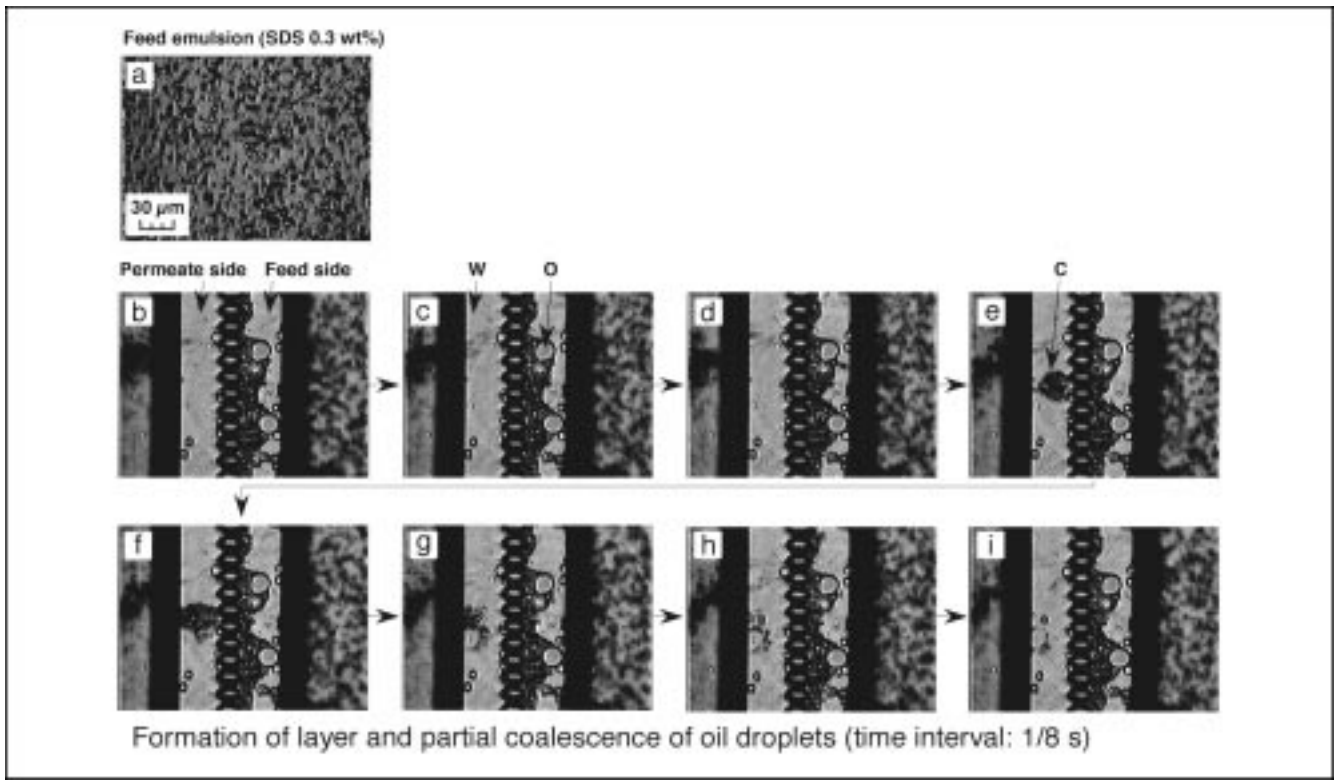

Figure 5. O/W (triolein/water containing 0.3 wt. % SDS) emulsion permeating through hydrophobic microchannels at 8.8 kPa (head difference: 0.9 m).

W, O, and C denote water, oil, and a cluster of oil droplets, respectively.

In additional, a change in the interfacial free energy by adsorption is also a large factor, which is discussed later.

Demulsification using hydrophobic membrane

The O/W (triolein/water containing 0.1 or 0.3 wt. % SDS) emulsions were filtered with PTFE membranes of several pore sizes (10, 5 and 1 μm) at several operating pressures (25, 50 and 100 kPa). Figure 6 shows the time course of flux in the filtration of O/W emulsion with a 5-μm PTFE membrane. When the SDS concentration was 0.1 wt. %, the flux was almost twice compared to that with 0.3 wt. % SDS at 25 kPa. The effect of the pressure on the flux was investigated with the SDS concentration of 0.3 wt. %. As expected, higher fluxes were obtained at higher pressures. For example, after 40 min, the fluxes at 25, 50 and 100 kPa were 2.9, 8.5 and 16.3×10^{-6} $m^3\cdot m^{-2}\cdot s^{-1}$, respectively. In every case, it took a few minutes to obtain a permeate because the membrane was hydrophobic and not easily wetted with continuous phase water. After breakthrough, the flux fluctuated but gradually decreased. The temporary increase in the flux was possibly caused by the intermittent release of coalesced oil from the membrane pores, and the subsequent gradual decrease in the flux may have resulted from an increase in the coalesced oil in the membrane pores.

Table 1 summarizes the weights of water and oily residue and the wt. % of the residue in the top and bottom fraction of the permeate with several PTFE membranes under various conditions. The main component of the residue is oil (triolein) on the basis of the ratio of oil (5 wt. %) and SDS (0.1 or 0.3 wt. %). In all cases, the permeate separated into two phases, an oily one (top fraction) and an aqueous one (bottom fraction). Every PTFE membrane had selectivity for the dispersed phase, oil, since the total oil contents in permeate were consistently higher than the initial oil content in the feed, 5 wt. %. The feed composition must have been depleted of oil, since a dead-end batch cell was used. The most complete phase separation was achieved when the SDS concentration was 0.1 wt. %. The top fraction contained more than 90 wt. % oil, while the bottom fraction contained less than 0.3 wt. % oil. With the SDS concentration of 0.3 wt. %, the emulsion was more stable and the content of the oil in the top fraction decreased to a value between 60 and 70 wt. % with either a 5- or a 10-μm membrane. The droplet stability is affected by the difference in the interfacial free energy. When an oil droplet of the radius, r, adsorbed on a membrane surface with the contact angle, θ, a change in the surface free energy, ΔE, is described with the following equations:

$$\Delta E = (\gamma_{SW} - \gamma_{SO})\, A_2 + \gamma_{OW}(S_1 - S_2), \tag{1}$$

where γ_{SW}, γ_{SO}, and γ_{OW} are the interfacial tensions between a membrane surface and water, a membrane surface and oil, and oil and water, respectively. S_1, S_2, and A_2 are the surface area of an original droplet, a partial surface area in contact with the water of the droplet adsorbed on a membrane, and a partial surface area in contact with the membrane of the droplet, respectively. Using the Young equation, Eq. 1 is rewritten

$$\Delta E = \gamma_{OW}(A_2 \cos\theta + S_1 - S_2). \tag{2}$$

Assuming the shape of oil adsorbed on the membrane surface is a part of a sphere, S_1, S_2, and A_2 are obtained using r and θ:

$$S_1 = 4\pi r^2 \tag{3}$$

$$S_2 = 2\pi(1-\cos\theta)\Psi r^2 \tag{4}$$

$$A_2 = \pi \sin^2\theta\, \Psi r^2 \tag{5}$$

$$\Psi = 4^{2/3}(2-3\cos\theta+\cos^3\theta)^{-2/3}. \tag{6}$$

The interfacial tension, γ_{OW}, and the contact angle, θ, are experimentally obtained: $\gamma_{OW} = 1.4\times10^{-2}$ N/m, $\theta = 29.4$ at SDS concentration = 0.1 wt. %; $\gamma_{OW} = 4.7\times10^{-3}$ N/m, $\theta = 32.5$ at SDS concentration = 0.3 wt. %. When the SDS concentration is 0.3 wt. %, ΔE for a droplet of 1 μm in radius, r, is calculated with Eqs. 2–6 as 4.4×10^{-14} N·m, which is one third of that at 0.1 wt. % and mostly corresponds with the difference in the interfacial tension. Smaller ΔE implies that the initial state is more stable and the transition of the state hardly occurs. Once a droplet is adsorbed on the membrane, it should be coalesced for detachment, because the interfacial free energy per unit volume is proportional to the reciprocal of the radius.

An increase in the oil residue to the bottom fraction was observed with a 5-μm membrane at 100 kPa. Assuming that droplets coalesce and cleave alternately in passing through the membrane, the operating pressure should be greater than the internal pressures of the droplets regenerated by the cleavage. The internal pressure (ΔP_{int}) is calculated with the

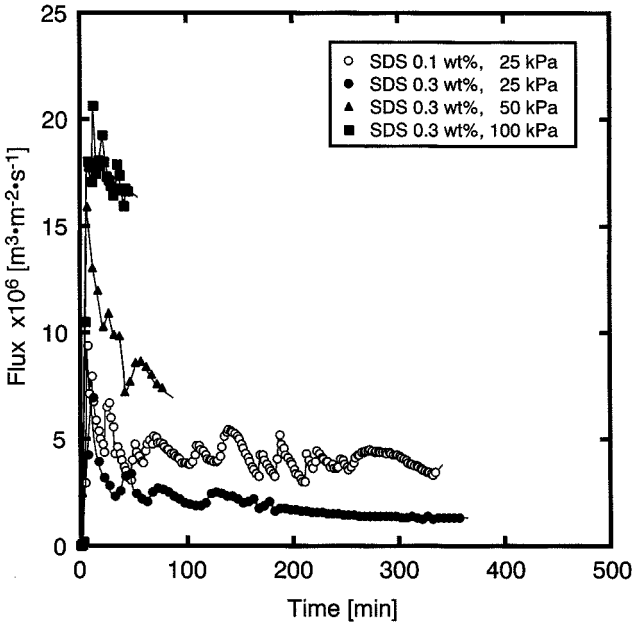

Figure 6. Time course of flux in filtration of O/W emulsion with a 5-μm PTFE membrane.

Table 1. Weights of Water and Oily Residue,* and Wt. % of Residue in Top, Bottom and Total Fractions of Permeate with Several PTFE Hydrophobic Membranes

SDS Conc. [wt. %]	Memb. Pore Size [μm]	Pres. [kPa]	Fraction	Mass of Water (A) [10^{-3} kg]	Mass of Oily Residue (B) [10^{-3} kg]	Permeate [wt. %]	Oily Residue* $B/(A+B)$ [wt. %]
0.1	5	25	Top	0.634	6.5	10.65	91.11
			Bottom	59.7	0.178	89.35	0.30
			Total	60.334	6.678	100.00	9.97
0.3	1	100	Top	0.49	2.11	4.76	81.15
			Bottom	51.1	0.9	95.24	1.73
			Total	51.59	3.01	100.00	5.51
	5	25	Top	3.93	7.81	19.07	66.52
			Bottom	49.4	0.41	80.93	0.82
			Total	53.33	8.22	100.00	13.35
		50	Top	4.27	8.89	19.81	67.55
			Bottom	52.9	0.361	80.19	0.68
			Total	57.17	9.251	100.00	13.93
		100	Top	1.21	2.04	6.49	62.77
			Bottom	45.4	1.44	93.51	3.07
			Total	46.61	3.48	100.00	6.95
	10	25	Top	3.84	7.31	17.24	65.56
			Bottom	52.7	0.821	82.76	1.53
			Total	56.54	8.131	100.00	12.57
		50	Top	3.04	6.4	13.90	67.80
			Bottom	57.5	0.989	86.10	1.69
			Total	60.54	7.389	100.00	10.88
		100	Top	3.23	6.37	14.75	66.35
			Bottom	54.4	1.09	85.25	1.96
			Total	57.63	7.46	100.00	11.46
	1-5-10	100	Top	1.43	6.86	13.20	82.75
			Bottom	54.4	0.108	86.80	0.20
			Total	55.83	6.968	100.00	11.10

*Oily residue consists of sunflower oil and surfactant SDS.

Young–Laplace equation:

$$\Delta P_{\text{int}} = 2\gamma_{\text{OW}}/r. \tag{7}$$

The minimum size of the regenerated droplets is then determined by the operating pressure; 0.75 μm for 25 kPa, 0.38 μm for 50 kPa, and 0.19 μm for 100 kPa. At 25 kPa, the minimum size of the droplets is similar to that of the original droplets, which suggests that the cleavage is less effective than coalescence. On the contrary, at 100 kPa the cleavage is considered to be more effective than coalescence. However, the droplet regeneration also includes a size effect of the membrane pores. If a membrane has large pores and a loose matrix like the 10-μm membrane, the cleavage effect is small even at a high pressure.

The time course of the flux in the filtration of the O/W emulsion with a 10-μm PTFE membrane is shown in Figure 7. The fluxes after 10 min were roughly linear to the pressures and more than 3 times higher than those with 5-μm membranes at the same pressure. As shown in Table 1, the operating pressure has little effect on the composition of the permeate over the range of 25–100 kPa for the 10-μm membrane. It is thought that cleavage is less effective than the coalescence due to a loose matrix of the 10-μm membrane. With a 1-μm membrane, the emulsion breakdown ability was strong and the content increased to 80 wt. %; however, the

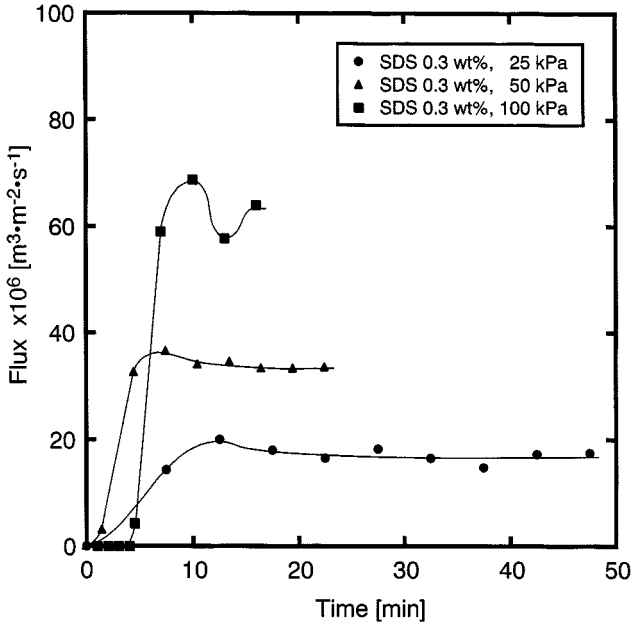

Figure 7. Time course of flux in filtration of O/W emulsion with a 10-μm PTFE membrane.

amount of oil (2.11×10^{-3} kg) was only about one third of that with the 10-μm membrane (6.37×10^{-3} kg) owing to a decrease in the growth space of the coalesced oil in the membrane pores.

Figure 8 shows the proposed phase-inversion and phase-separation mechanisms of the O/W emulsion permeating through the single layer (Figures 8a, 8b) and multilayer (Figure 8c) PTFE membranes. The single-layer, 1-μm PTFE membrane has good breakdown ability for O/W emulsion droplets; however, continuous space for the coalesced oil is small (Figure 8a). The single-layer, 10-μm PTFE membrane has large continuous space, but some oil droplets partially permeate without coalescence (Figure 8b). It is assumed that the multilayer, 1-5-10-μm membrane is effective in completely breaking down large amounts of emulsion to exploit the breakdown potential of the 1-μm membrane and the growth space of the 5- and 10-μm membranes (Figure 8c). The experimental result with the multilayer membrane is shown in Table 1. The oil amount in the top fraction increased to a similar level to that of the 10-μm single membrane, but the oil concentration in the top fraction was higher than 80 wt. %, and that in the bottom fraction was below 0.2

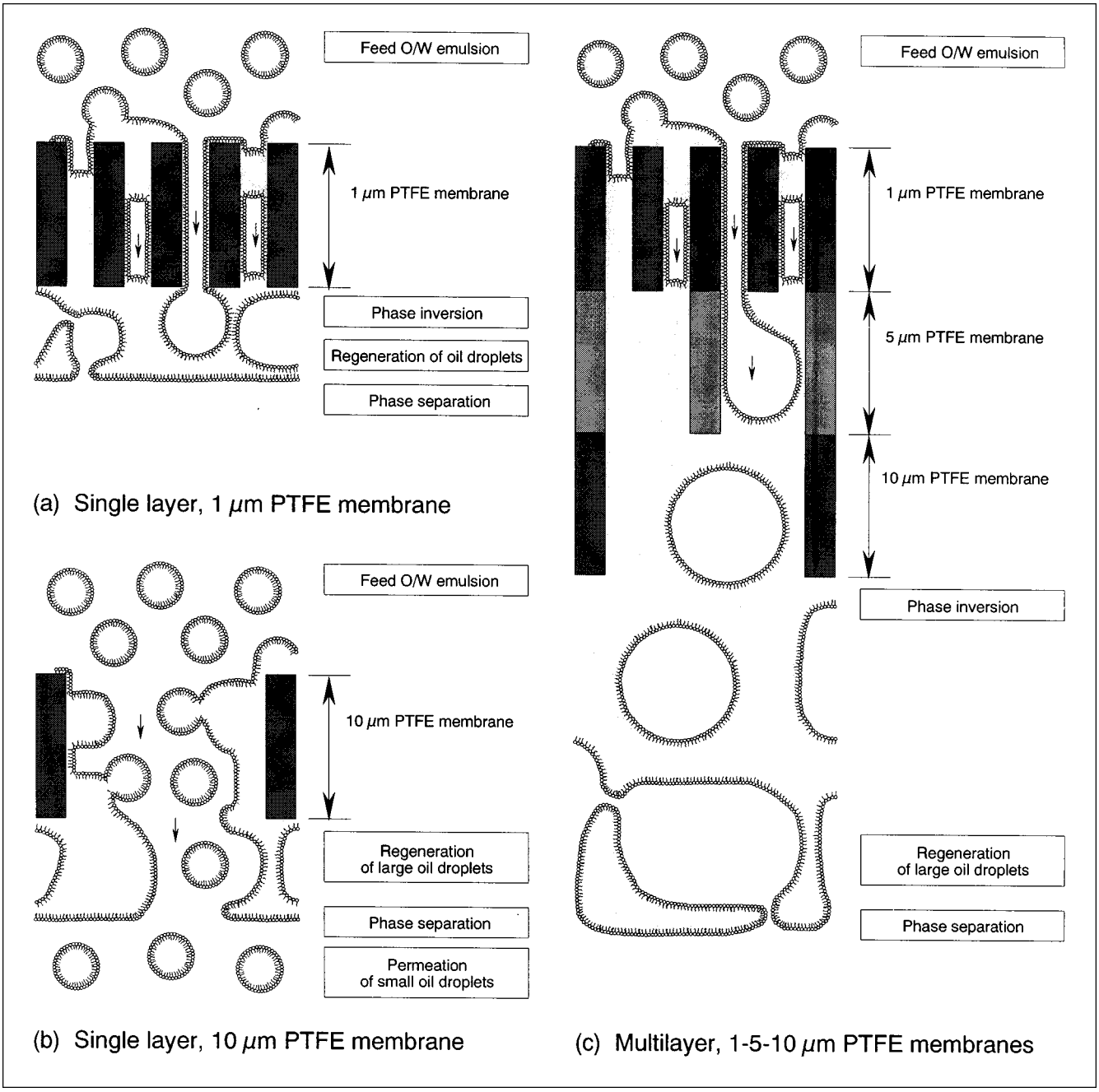

Figure 8. Phase inversion and separation mechanism of O/W emulsion permeating through single layer (a, b) and multilayer (c) PTFE membranes.

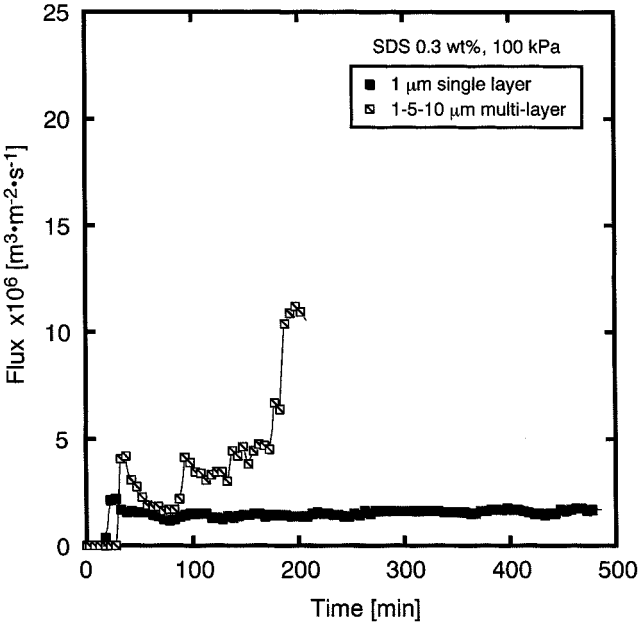

Figure 9. Time course of flux in filtration of O/W emulsion with 1-μm single layer and 1-5-10-μm multilayer PTFE membranes.

wt. %. Figure 9 shows the time course of the flux in the filtration of the O/W emulsion with the 1-μm single-layer and 1-5-10-μm multilayer PTFE membranes. With the 1-μm single-layer membrane, the flux was below 2×10^{-6} $m^3\cdot m^{-2}\cdot s^{-1}$, even at 100 kPa. It is remarkable that the flux with the multilayer membrane gradually increased with fluctuation. The resistance of the multilayer membrane itself must be greater than that of the single 1-μm membrane, since it consists of the sum of the resistances of each membrane layer. A possibility is that with the single 1-μm membrane the coalesced oil blocks the membrane pores and becomes a barrier to the water flow; however, with the multilayer membrane, coalesced oil moved smoothly to the downstream because the membrane had large continuous spaces for oil, and water paths might be gradually built during the filtration. This implies that detachment of the oil drops from the permeate side of the membrane is difficult in the case of the single-layer 1-μm membrane on the basis of the Young–Laplace equation applied in the bubble point and the mercury intrusion methods in which higher pressures are necessary to breakthrough smaller pores. The flux gradually increased as the 5- and 10-μm layers were wetted by the oily phase, while the flux with the multilayer membrane was initially of the same order as the single-layer 1-μm membrane.

Conclusions

The phase-inversion phenomena of the O/W emulsion permeating through hydrophobic micropores were visualized using a silicon microchannel plate that was modified with a hydrophobic silane coupler reagent and a microscope video system. Oil droplets coalesced on the hydrophobic microchannel surface and permeated to form a continuous oil phase at the outlet of the microchannel, while water was repelled from the surface. Irregular-sized water droplets were created at the outlet. The microchannel plate has a high potential to be a strong demulsification device if the production cost is reduced so it is similar to that of a polymeric membrane.

O/W emulsions were filtered with polytetrafluoroethylene (PTFE) hydrophobic membranes of several pore sizes (10, 5 and 1 μm) at several operating pressures (25, 50 and 100 kPa). In all cases, the permeates separated into an oily and an aqueous phase. When the SDS concentration was 0.1 wt. % the phase separation was almost complete with a 5-μm PTFE hydrophobic membrane: the oily (top) phase contained more than 90 wt. % of oil, while the aqueous (bottom) phase contained less than 0.3 wt. % of oil. The emulsion containing 0.3 wt. % SDS was more stable; however, the proposed method using multilayer 1-5-10-μm membranes enabled good phase separation: the oily phase contained more than 80 wt. % of oil, while the aqueous phase contained less than 0.2 wt. % of oil. A remarkably high flux was obtained with this multilayer membrane.

Acknowledgments

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