Chapter 6

Characterization of Straight-Through Microchannel Emulsification

6.1 Effect of Elongation and Size of Oblong Straight-Through Microchannels on Droplet Formation

6.1.1 Introduction

In Chapter 5, we reported that an oblong straight-through MC exhibited an excellent performance in the production of monodisperse droplets on a 10-μm scale. The elongated cross-sectional shape of the straight-through MC was found to contribute to the spontaneous droplet formation from the channels. Straight-through MC emulsification using the oblong straight-through MC demonstrated the stable production of monodisperse emulsion droplets at a maximum dispersed phase flux of 65 l/(m^2 h) (droplet formation volume rate of 6.5 ml/h per plate) much greater than that in MC emulsification. The geometry of the oblong straight-through MC, such as the channel elongation and channel size, is supposed to affect the droplet formation behavior and the resultant droplet size and size distribution. It is necessary for optimization of the straight-through MC emulsification process that we understand the droplet formation behavior from the oblong straight-through MCs with different elongations and sizes.

In Chapter 6.1, the effects of the elongation and size of the oblong straight-through MCs on the oil droplet formation behavior and on the resultant droplet size and size distribution were investigated. The droplet formation characteristics using an oblong straight-through MC with an improved elongation were also investigated.

6.1.2 Materials and Methods

Materials

Soybean oil (Wako Pure Chemical Ind., Osaka, Japan) was used as the dispersed phase of the emulsification system, and 1.0 wt.% sodium dodecyl sulfate [SDS; hydrophilic lipophilic balance (HLB), 40] (Wako Pure Chemical Ind., Osaka, Japan) aqueous solution as the continuous phase.

Silicon straight-through MC plate

Figure 6.1.1 schematically depicts the straight-through silicon MC plate used in Chapter 6. A 5-inch silicon wafer with a 400 μm-thickness was used to fabricate the

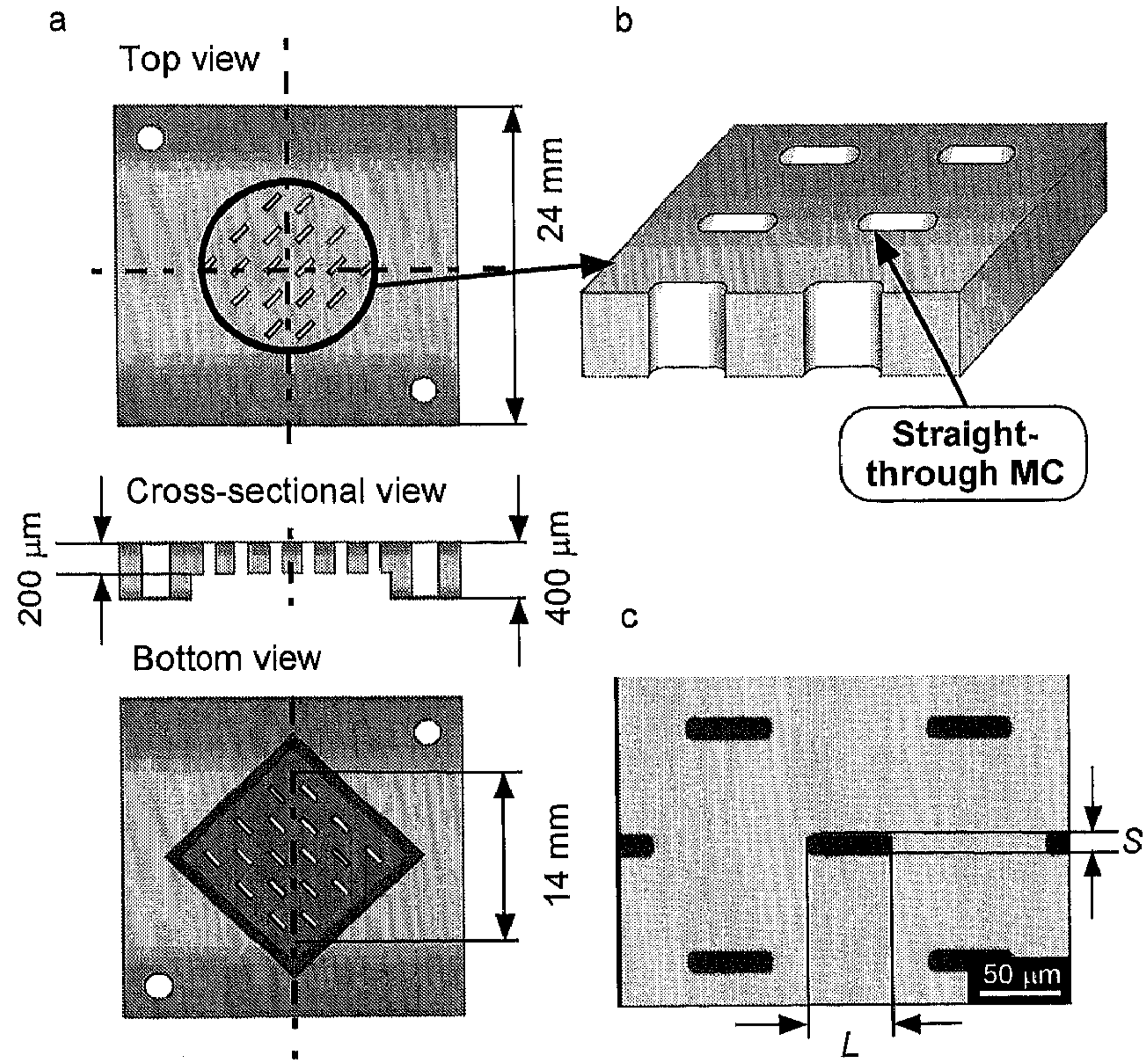

Fig. 6.1.1 Silicon straight-through MC plate. (a) Schematic drawing of the top view, and bottom view of the straight-thorugh MC plate; (b) Schematic drawing of a straight-through MC; (c) a SEM photograph of an oblong straight-through MC.

straight-through MC plates used in this Chapter. The fabrication process of the straight-through MC plate was described in detail in Chapter 5.2. The fabricated plate has a hydrophilic surface, which is attributable to a hydrophilic silicon oxide layer. The straight-through MC plate measures 24 mm × 24 mm × 0.4 mm, with 1.5-mm diameter holes to feed the dispersed phase. Oblong channels of uniform size were fabricated in a 10-mm square in the center of this plate with a 0.2 mm-thickness. They was positioned at channel intervals long enough to prevent contact between droplets growing from adjacent channels. The measured effective channel area was 1.0×10^{-4} m^2. Each oblong straight-through MC is identified by its longer line (L) and shorter line (S) (Fig. 6.1.1c). Four types of the straight-through MC plates (TMC-A, TMC-B, TMC-C, and TMC-D) were newly designed and fabricated. Table 6.1.1 presents the dimensions of the oblong straight-through MCs.

Straight-through MC emulsification system

Figure 6.1.2 schematically illustrates the straight-through MC emulsification system used in this chapter and the flow mechanism through the straight-through MC in the module. Details of the straight-through MC emulsification system were described in Chapter 5.2.

Straight-through MC emulsification

The straight-through MC plate was presoaked in the continuous phase with ultrasonification for 20 min and was then mounted in the module, which was initially filled with the continuous phase. Two syringe pumps (505U, Watson-Marlow Ltd., Cornwall, UK) were connected to the inlets of the module to feed the dispersed phase and the continuous phase. The dispersed phase, which was fed into the module, achieved the backside of the straight-through MC plate. Droplet formation then initiated by forcing the dispersed phase through the straight-through MC into the continuous phase. The droplets formed were recovered by the controlled continuous phase flow. All experiments were

Table 6.1.1 Dimensions of silicon oblong straight-through MCs.

Channel type	Channel equivalent diameter[a] (μm)	Longer channel length L (μm)	Shorter channel length S (μm)	Channel elongation L/S (-)
TMC-A1	17.8	17.9	17.7	1.0
-A2	18.4	25.2	13.3	1.9
-A3	17.6	32.8	12.0	2.7
-A4	17.1	40.7	10.8	3.8
-A5	18.2	48.8	11.2	4.4
TMC-B	16.0	9.6	48.7	5.1
TMC-C1	53.7	54.0	53.3	1.0
-C2	54.7	77.9	42.1	1.9
-C3	54.0	101.4	36.8	2.8
-C4	54.1	126.4	35.0	3.6
-C5	55.1	151.0	33.7	4.5
TMC-C'5	69.2	156.2	44.1	3.5
TMC-D1	155.1	156.2	154.1	1.0
-D2	157.1	229.4	119.3	1.9
-D3	157.1	304.4	105.9	2.9
-D4	160.0	379.7	101.3	3.7
-D5	160.6	455.0	97.5	4.7
TMC-D'5	202.2	505.5	126.8	4.0

[a]Channel equivalent diameter is defined as four times the cross-sectional area divided by the wetted perimeter of the channel.

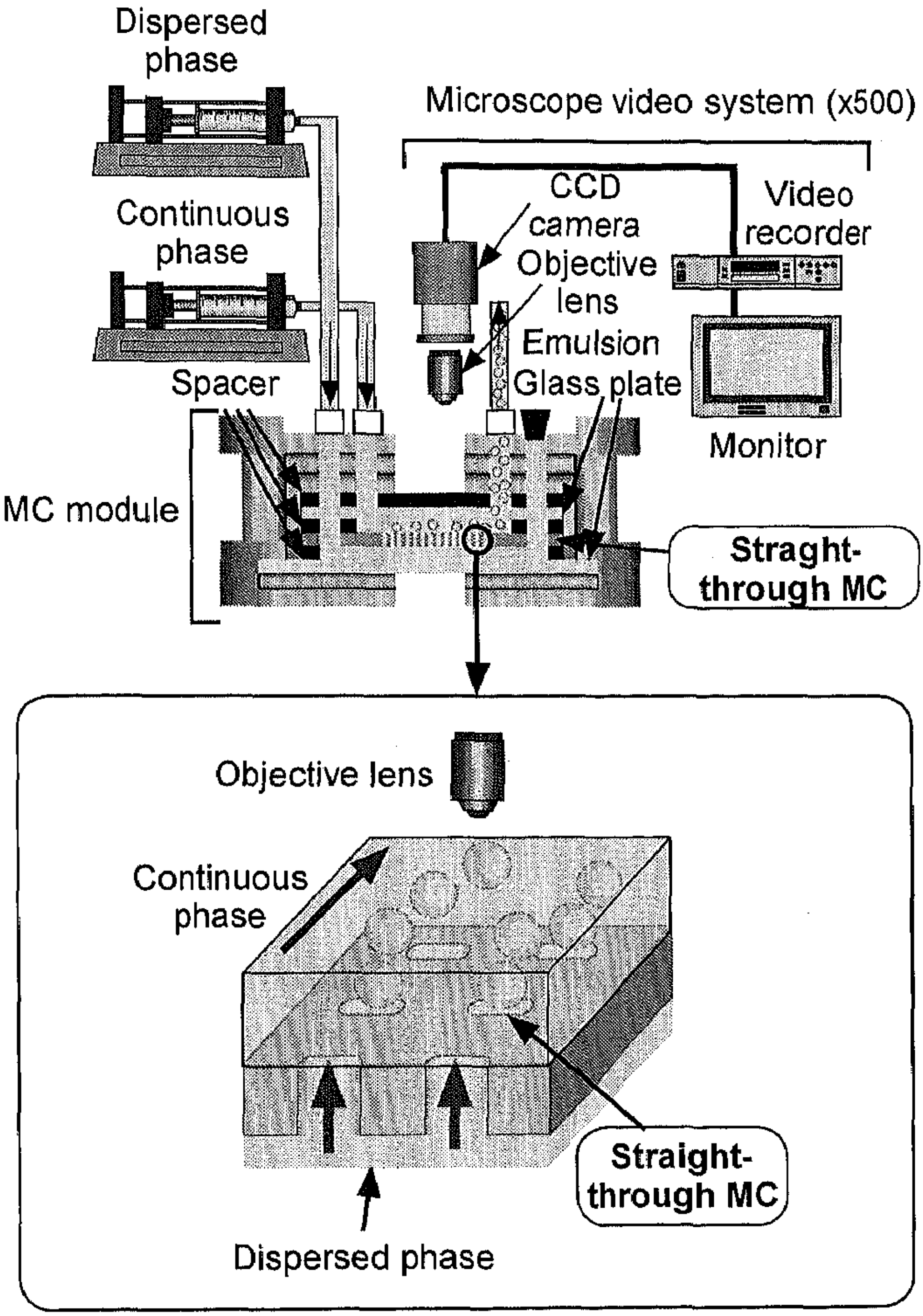

Fig. 6.1.2 Experimental setup and flow through the straight-through MC in the module.

conducted at ambient temperature, approximately 25°C.

Measurements and analysis

The droplet formation behavior from the straight-through MC was analyzed from video images taken during the experimental runs. The average droplet diameter and coefficient of variation of the prepared emulsions were determined by analyzing photographs of 200 droplets that were captured on a personal computer using image processing software (WinRoof, Mitani Co., Ltd, Japan). The coefficient of variation, which provides the degree of the droplet size distribution, was described in detail in Chapter 2.2.

6.1.3 Results and Discussion

Effect of elongation of oblong straight-through MC

The effect of the elongation of oblong straight-through MCs on the emulsification behavior was examined. TMC-A, used as the straight-through MC plate, has five oblong straight-through MCs with elongations of 1.0 to 4.4 and equivalent diameters of 17.1 to 18.4 μm (Table 6.1.1). Straight-through MC emulsification was performed at a continuous phase flow velocity between 0 and 12 mm/s and a dispersed phase flux of 10 $l/(m^2\ h)$ (droplet formation volume rate of 1.0 ml/h per plate). Figure 6.1.3 illustrates the typical behavior of droplet formation from the oblong straight-through MCs with different channel elongations at a continuous-phase flow velocity of 1.2 mm/s. In the oblong straight-through MCs with elongations of 1.0 and 1.9 (TMC-A1 and TMC-A2), the dispersed phase that broke through the channels continued growing up to 400 μm or more, and then the continuous phase flow made the dispersed phase droplets detach from the channel tip (Fig. 6.1.3a). The oblong straight-through MCs yielded almost uniformly sized oil droplets from each channel, whereas their diameter depended on the site of the channels. This unstable droplet formation driven by the continuous phase flow has a similar tendency to oil droplet formation from the circular straight-through MC described

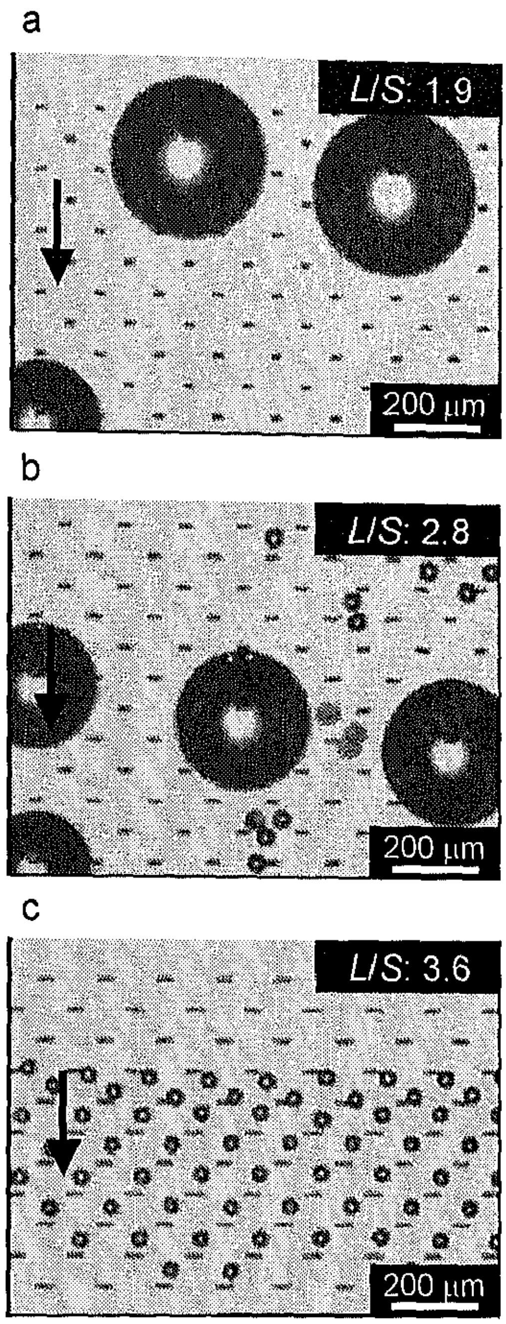

Fig. 6.1.3 Microscopic photographs of droplet formation from oblong straight-through MCs with different channel elongations for soybean oil / water (1.0 wt.% SDS) system. (a) Continuous droplet growth; (b) combination of spontaneous droplet formation and continuous droplet growth; (c) spontaneous droplet formation with uniform droplet diameter.

in Chapter 5.4. In addition, the diameter of the droplets formed using TMC-A1 and TMC-A2 showed the continuous-phase flow velocity dependence; their diameter decreased with the increase in the continuous-phase flow velocity (data are not shown). We thus found that it was difficult to form monodisperse droplets from the straight-through MCs with small elongations. In the straight-through MC with elongation of 2.8 (TMC-A3), besides the continuous phase flow-driven droplet formation, the spontaneous formation of oil droplets was observed from some channels (Fig. 6.1.3b). Each of the working channels did not cause transition between the spontaneous droplet formation and the continuous phase flow-driven droplet formation. The spontaneously formed droplets were of uniform size and had an average diameter of about 46 μm. Microscopic observations of the droplet formation process showed that the channels that caused the continuous phase flow-driven droplet formation seem to have slightly smaller elongations. The oblong straight-through MC with elongation of 3.1 demonstrated spontaneous formation of monodisperse oil droplets from all the channels working (see Chapter 5.4). The results obtained using TMC-A3 indicate that there exists a transition elongation between the spontaneous droplet formation and the continuous phase flow-driven droplet formation. In the oblong straight-through MCs with the elongations of 3.6 and 4.4 (TMC-A4 and TMC-A5), uniformly sized oil droplets were spontaneously formed from all the channels working (Fig. 6.1.3c), similarly like the case using the oblong straight-through MC described in Chapter 5.4. The average droplet diameter and coefficient of variation of the droplets formed were 41.9 μm and 1.9% for TMC-A4 and 48.3 μm and 2.3% for TMC-A5, which verifies their monodispersity. The resulting droplet diameters were analogous to the longer channel length for both TMC-A4 and TMC-A5. They were independent of the applied continuous-phase flow velocity. We thus revealed that the elongation exceeding a threshold, which was about three, is required to stably form monodisperse droplets from the oblong straight-through MC with equivalent diameters of about 20 μm.

Effect of dispersed phase flux on straight-through MC emulsification

The effect of the dispersed phase flux on the straight-through MC emulsification behavior was also investigated using TMC-B. A newly fabricated TMC-B with an equivalent diameter of 16.0 μm possesses a channel elongation of 5.1, which is large enough to stably produce monodisperse droplets. Figure 6.1.4 depicts microscopic photographs of the droplet formation behavior from TMC-B. Straight-through MC emulsification using TMC-B was started at a dispersed phase flux of 10 l/(m^2 h) (droplet formation volume rate of 1.0 ml/h per plate). The microscopic photograph in Fig. 6.1.4a confirms the spontaneous formation of uniformly sized oil droplets from TMC-B. The average diameter and coefficient of variation of the resulting droplets were 39.1 μm and 2.5%, respectively. The dispersed phase flux was then increased in steps. We observed that TMC-B stably yielded monodisperse oil droplets in a range of the dispersed phase flux below 60 l/(m^2 h) (droplet formation volume rate of 6.0 ml/h per plate) (Figs. 6.1.4a and b). This region was defined as the "size-stable zone". The average diameter and coefficient of variation of the resultant droplets was independent of the dispersed phase flux in the size-stable zone, as shown in Fig. 6.1.5. Droplet formation rate, which increased with the increase with the dispersed phase flux, was approximately 6 droplets/s at a dispersed phase flux of 60 l/(m^2 h). TMC-B commenced oil droplet formation including larger droplets at a dispersed phase flux of 70 l/(m^2 h) (droplet formation volume rate of 7.0 ml/h per plate) (Fig. 6.1.4c). All the droplets that grew from TMC-B were spontaneously detached from the channels. This region, called "size-expanding zone 1", existed between the dispersed phase flux of 70 and 90 l/(m^2 h). Their average diameter and coefficient of variation in the size-expanding zone increased with the increase the dispersed phase flux, achieving up to 50.1 μm and 14.5% at a dispersed phase flux of 90 l/(m^2 h) (Fig. 6.1.5). The diameter distribution of the droplet formed thus tended to become broader in the size-expanding zone. A drastic increase in the diameter of the resultant droplets was observed at a dispersed phase flux of 100 l/(m^2 h) (droplet formation volume rate of 10 ml/h per plate), as depicted in Fig. 6.1.4d. A polydisperse emulsion with an average droplet diameter of

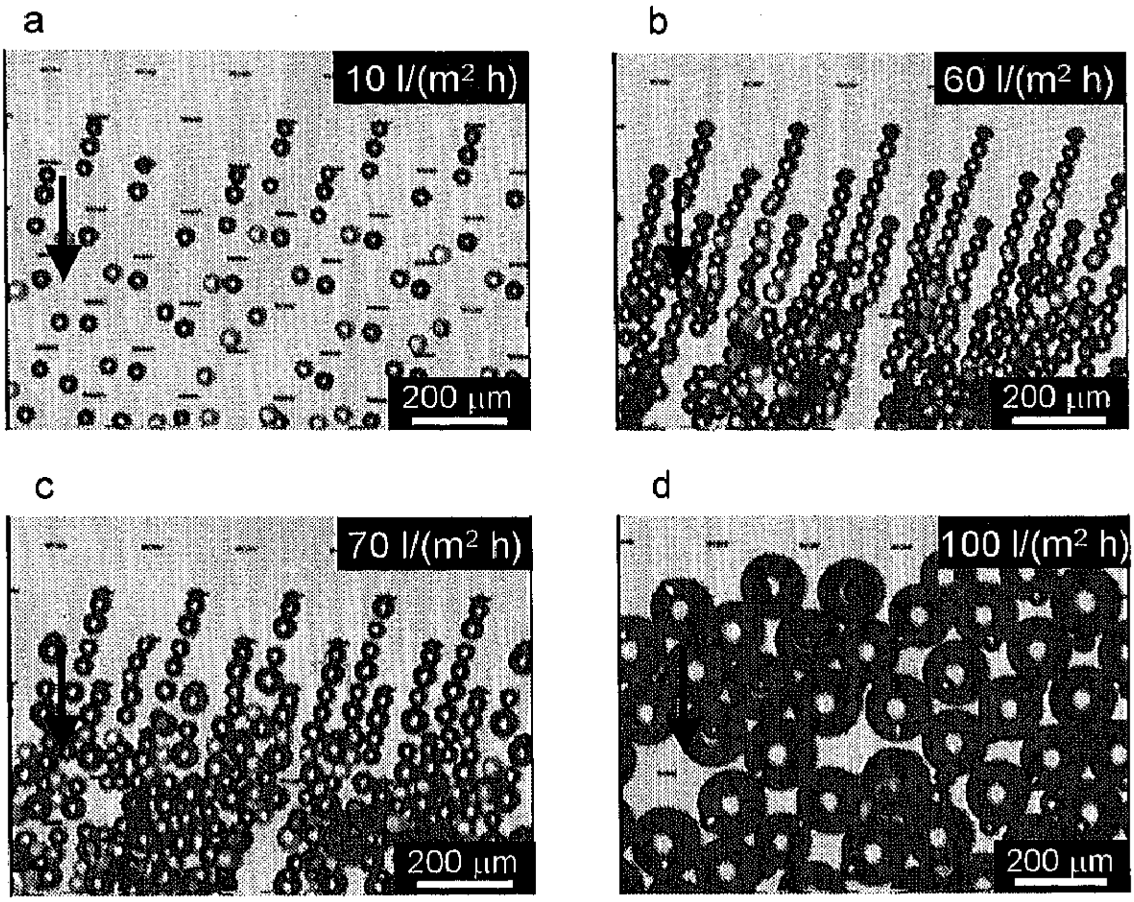

Fig. 6.1.4 Microscopic photographs of droplet formation from TMC2-1 for soybean oil / water (1.0 wt.% SDS) system. (a), (b) Size-stable zone; (c) size-expanding zone 1; (d) size-expanding zone 2. A dispersed phase flux of 60 l/(m^2 h) corresponds to a droplet formation volume rate of 6.0 ml/h per plate.

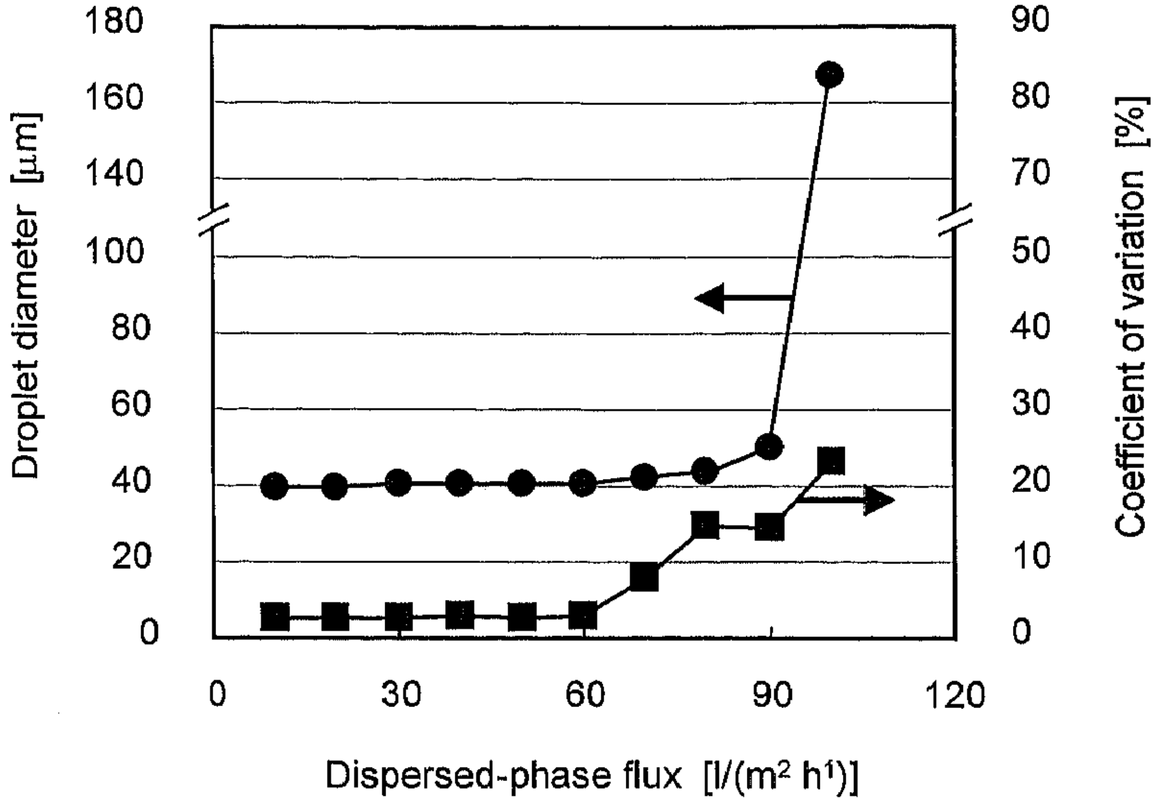

Fig. 6.1.5 Effect of dispersed phase flux on average diameter and coefficient of variation of droplets formed using TMC-B for soybean oil/1.0 wt.% SDS aqueous solution system. A dispersed phase flux of 60 l/(m^2 h) corresponds to a droplet formation volume rate of 6.0 ml/h per plate.

168 μm and a coefficient of variation of 23% was obtained in this case. This region was defined as the "size-expanding zone 2". Steric hindrance among the neighboring dispersed phase droplets restricted their further growth and forced them to detach from the channel tip. No spontaneous droplet formation from the channels was observed in this zone. Tong *et al.* (2001) have reported that MC emulsification using stainless steel MCs with an equivalent diameter of 20.4 μm demonstrated the size-stable zone of 0.8 to 1.95kPa applied pressures and the size-expanding zone of 1.95 to 6.94 kPa applied pressures. It should be noted that the space at the channel outlet in the stainless steel MC was partially restricted by an attached glass plate, which differs from that in the straight-through MC. The preceded results verified that the oblong straight-through MC with an appropriate elongation and an equivalent diameter of about 20 μm allows stable formation of monodisperse oil droplets in a wide range of the dispersed phase flux.

Effect of channel size of oblong straight-through MC

We newly designed two straight-through MC plates, TMC-C and TMC-D (Table 6.1.1). Each of the straight-through MC consisted of five oblong straight-through MCs with equivalent diameters of about 55 μm for TMC-C and about 160 μm for TMC-D. The applied continuous-phase flow velocity and dispersed phase flux were 0 and 1.2 mm/s and 10 $l/(m^2\ h)$ (droplet formation volume rate of 1.0 ml/h per plate), respectively. The oil droplet formation behavior using the TMC-A series with equivalent diameters of about 20 μm was described in detail in the above sections.

The oil droplet formation behavior using the TMC-C series was first investigated. Each oblong straight-through MC in the TMC-C series consists of four straight cross-sectional lines. Figs. 6.1.6a and b depict microscopic photographs of the droplet formation process for TMC-C5. TMC-C5 with the largest elongation of 4.5 in the TMC-C series was expected to have the best potential to perform successful straight-through MC emulsification. However, all of oil droplets that passed through TMC-C5 continued growing up to over 500 μm, then being forced to detach from the

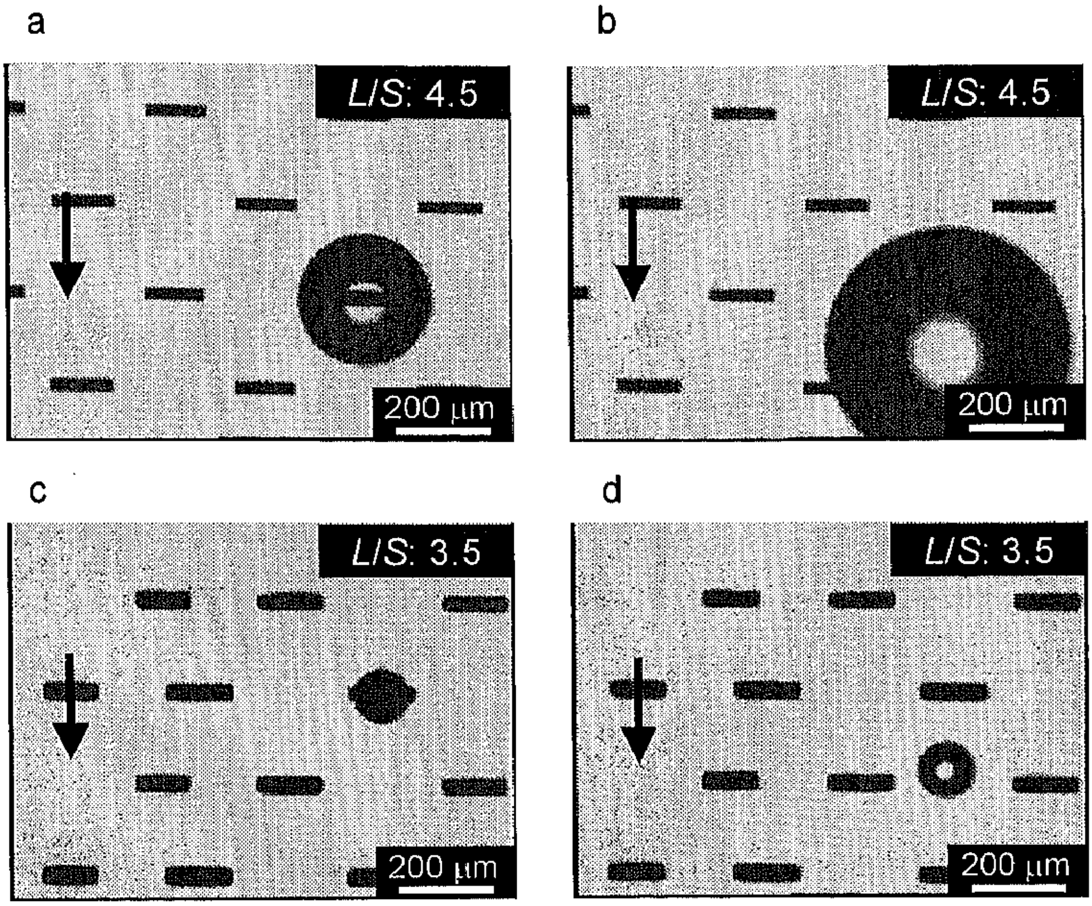

Fig. 6.1.6 Microscopic photographs of droplet formation from oblong straight-through MCs with smooth and distorted cross-sectional lines for soybean oil / water (1.0 wt.% SDS) system. (a), (b) Continuous phase flow-driven droplet formation from TMC-C5; (c), (d) spontaneous droplet formation from TMC-C'5.

channels by the continuous phase flow. The other TMC-C series with smaller elongations also exhibited the unstable continuous phase flow-driven droplet formation. Thus, the TMC-C series with equivalent diameters of about 55 μm had a difficulty in spontaneously producing uniformly sized oil droplets regardless of the value of their elongations. We found that an increase in the size of the oblong straight-through MC tends to make straight-through MC emulsification unstable.

An earlier study in MC emulsification reported that stainless steel MCs with an equivalent diameter of 40.2 and 79.0 μm stably formed monodisperse emulsion droplets (Tong *et al.*, 2001). On the other hand, a silicon MC with a terrace at the channel outlet unstably formed the polydisperse emulsion droplets (Sugiura *et al.*, 2000). Rough cross-sectional lines of the stainless steel MCs differed from those of the MC and the TMC-C series. We assumed that an oblong straight-through MC with rough cross-sectional lines might allow the stable formation of monodisperse droplets, even though its equivalent diameter was almost the same as that of the TMC-C series. A sensitive deep silicon etching process described in Chapter 5.2 sometimes fabricates oblong straight-through MCs with distorted cross-sectional lines. When fabricating the straight-through MC plate (TMC-C), the oblong straight-through MCs with distorted cross-sectional lines, named the TMC-C' series, were also fabricated (Table 6.1.1). The oil droplet formation behavior using the TMC-C' series was then investigated. The TMC-C' series with small elongations resulted in the continuous droplet growth and subsequent continuous phase flow-driven droplet detachment. In TMC-C'5 with a large elongation of 3.5, uniformly sized oil droplets were stably formed from the channels even without the continuous phase flow (Fig. 6.1.6c). This result shows that the rough cross-sectional lines of the oblong straight-through MC promote droplet detachment from the channels and enables the spontaneous formation of monodisperse emulsions with droplets as large as 100 μm.

Difference in the droplet formation behavior between the TMC-C series and TMC- C' series can be explained as follows. The transfer of the continuous phase to the space between the dispersed phase and the channels is required to complete droplet detachment from the channels. However, the narrow space between the dispersed phase and the channels in the TMC-C series makes it difficult to transfer the continuous phase to the space. Droplet detachment from the TMC-C series takes time due to the narrow space. This prevents the spontaneous droplet detachment and leads to the continuous phase flow-driven droplet detachment. In contrast, the distorted cross-sectional lines in the TMC-C' series provide the micro-space for the continuous phase between the dispersed phase and the channels. We believe that the micro-space rapidly completes the transfer of the continuous phase to the space and allows the spontaneous droplet detachment from the TMC-C' series.

The droplet formation behavior using the TMC-D series was next investigated. Figure 6.1.7a depicts a microscopic photograph of the droplet formation process for TMC-D5. Although oil droplets the broke through the channel in all the TMC-D series grew up to the clearance in the module (approximately 2.0 mm), little droplets detached from the channel tip during straight-through MC emulsification. Straight-through MC emulsification using the TMC-D' series with distorted cross-sectional lines was also conducted. Continuous droplet growth up to the clearance in the module, as depicted in Fig. 6.1.7b, was observed in all the TMC-D' series. This result indicates that the distorted cross-sectional lines of the oblong straight-through MC are no longer effective in spontaneously forming monodisperse droplets for the oblong straight-through MC with an equivalent diameter of about 160 μm.

The preceded results let us to find that the smaller the channel equivalent diameter, the easier the spontaneous formation of monodisperse droplets. We also found that the distortion of the cross-sectional lines of the straight-through MC contributes to the stable formation of monodisperse emulsion droplets in addition to its elongated cross section.

6.1.4 Conclusions

In Chapter 6.1, we have made clear that the elongations of oblong straight-through MCs

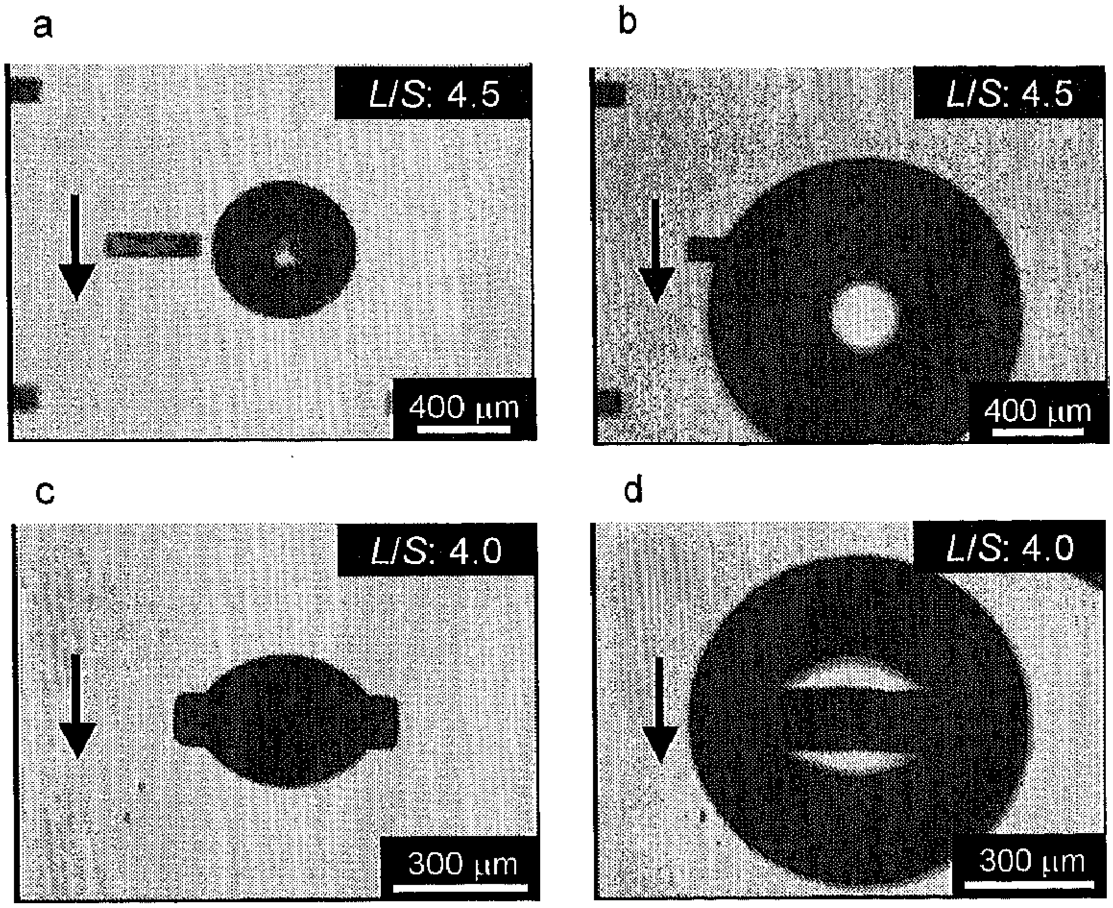

Fig. 6.1.7 Microscopic photographs of droplet formation from oblong straight-through MCs with smooth and distorted cross-sectional lines for soybean oil / water (1.0 wt.% SDS) system. (a), (b) Continuous phase flow-driven droplet formation from TMC-D5; (c), (d) continuous phase flow-driven droplet formation from TMC-D'5.

must exceed a threshold, e.g., three for the oblong straight-through MCs with equivalent diameters of about 20 μm, to stably form monodisperse emulsion droplets. Straight-through MC emulsification using TMC-B with an improved elongation showed a size-stable zone and size-expanding zones with an increase in the dispersed phase flux. Large oblong straight-through MCs have a difficulty in stably forming monodisperse emulsion droplets regardless the value of their elongations. TMC-C'5 with distorted cross-sectional lines in the large oblong straight-through MC stably formed uniformly sized oil droplets as large as approximately 100 μm. Thiindicates that the shape of the cross-sectional lines of the oblong straight-through MC is a factor greatly affecting the droplet formation behavior besides its elongation.

6.2 Effect of Surfactant Type on Droplet Formation in Straight-Through Microchannel Emulsification

6.2.1 Introduction

Surfactants play a very important role in the emulsification process. The principal role of surfactants is to enhance emulsion formation by diminishing interfacial tension and to stabilize the formed emulsions by inducing a repulsive force between droplets (Dickinson, 1992). Bancroft's rule states that the phase in which the surfactant is most soluble will form the continuous phase of an emulsion (McClements, 1999). Hence, water-soluble surfactants are generally used to make oil-in-water (O/W) emulsions, whereas oil-soluble surfactants are used to make water-in-oil (W/O) emulsions.

Earlier studies on membrane emulsification (Nakashima *et al.*, 1993, 2000) and microchannel (MC) emulsification (Tong *et al.*, 2000) reported that the type of the surfactants used, particularly the surfactant charge, significantly affected the droplet formation behavior. They also described that the surfactants suitable for membrane emulsification and MC emulsification must have the potential to prevent wetting of the dispersed phase on the membrane and channel surfaces.

Straight-through MC emulsification employs a micromachined emulsification device, a straight-through MC plate, with the negatively charged surface as well as membrane emulsification and MC emulsification. Therefore, the selection of surfactants is very important to stably form monodisperse emulsions by straight-through MC emulsification. In Chapter 6-2, the effect of the surfactant type on oil droplet formation behavior was investigated in straight-through MC emulsification using differently charged surfactants.

6.2.2 Materials and Methods

Materials

Soybean oil (Wako Pure Chemical Ind., Osaka, Japan) was used as the dispersed phase. MilliQ water (Millipore Co., Massachusetts, USA) was used to prepare all of the continuous phase solutions. Sodium dodecyl sulfate [SDS], polyoxyethelene (20) sorbitan monolaurate [Tween20; hydrophilic lipophilic balance (HLB), 13], cetyltrimethylammonium bromide [CTAB], and tri-n-octyl-methylammonium chloride

[TOMAC] (Wako Pure Chemical Ind., Osaka, Japan) were used as the surfactants.

Experimental setup

The straight-through silicon MC plate used in Chapter 6.2 was described in detail in Chapter 6.1.1. An oblong straight-through MCs (TMC-B) was used in Chapter 6.2. The dimensions of the straight-through MC are presented in Table 6.1.1. Details of the straight-through MC emulsification system were described in Chapter 5.2.

Straight-through MC emulsification

The surfactants used were dissolved into either water or soybean oil at a concentration higher than the critical micelle concentration (CMC). The straight-through MC emulsification procedures were described in detail in Chapter 6.1.

Measurements and analysis

The droplet formation from the straight-through MC was analyzed using video images taken during the experimental runs. Droplet size measurements were conducted by the method described in Chapter 5.2. The average droplet diameter and coefficient of variation of the prepared emulsions were calculated from the measured droplet diameters. The definition of the coefficient of variation was described in Chapter 2.2.

Interfacial tension measurements were conducted with a pendant drop method as described in detail in Chapter 2.2.

6.2.3 Results and Discussion

Straight-through MC emulsification using an anionic surfactant

The surfactant effect on the O/W straight-through MC emulsification was investigated using differently charged surfactants. Table 6.2.1 shows the experimental conditions, measured interfacial tensions and contact angles. Straight-through MC emulsification was carried out at a continuous-phase flow velocity of 1.2 mm/s and a dispersed phase flux

Table 6.2.1 Contact angle and interfacial tension of the experimental systems used.

Surfactant[a]	Condition	Contact angle[b] (deg)	Interfacial tension (mN/m)
SDS	1.0 wt% (W)[c]	145	4.0
Tween20	1.0 wt% (W)	142	1.9
CTAB	1.0 wt% (W)	134	<0.1
TOMAC	2.0 wt% (O)[d]	38	3.1

[a]SDS, sodium dodecyl sulfate; Tween20, polyoxyetylene (20) monolaurate;
CTAB, cetyltrimethylammonium bromide; TOMAC, tri-n-octylmethylammonium chloride.
[b]Contact angle between an oil droplet and the channel surface in the water phase.
[c]Dissolved in the continuous water phase.
[d]Dissolved in the dispersed oil phase.

of 10 l/(m^2 h) (droplet formation volume rate of 1.0 ml/h per plate), respectively. The oil droplet formation behavior using an anionic surfactant- (SDS) containing system was first investigated in straight-through MC emulsification and was described in detail in Chapter 6.1.3. In this case, the stable formation of monodisperse oil droplets was observed from all the channels working (Fig. 6.1.4). This phenomenon can be explained as follows. The electric repulsive interaction works between the negatively charged group of SDS and the channel surface with negative zeta potential, keeping the channel surface hydrophilic during straight-through MC emulsification. Maintaining the hydrophilicity of the channel surface is also a prerequisite for stable formation of emulsion droplets in membrane emulsification (Nakashima *et al.*, 1991; Katoh *et al.*, 1996) and MC emulsification (Tong *et al.*, 2000). We thus confirmed that an anionic surfactant (SDS)-containing system is appropriate for stable formation of monodisperse oil droplets in straight-through MC emulsification.

Straight-through MC emulsification using a nonionic surfactant

The oil droplet formation behavior using a nonionic surfactant- (Tween20) containing system was next investigated in straight-through MC emulsification. The microscopic photograph in Fig. 6.2.1a demonstrates the stable formation of uniformly sized oil droplets from the channels for Tween20-containing system. The resultant droplets had an average diameter of 38.6 μm and a coefficient of variation of 2.5%. Nonionic surfactants have no strong repulsion with the membrane surface, which differs from anionic surfactants. In contrast, the Tween20-containing systems exhibited a measured contact angle of 142°, which is sufficiently high to remain the channel surface hydrophilic. This suggests that straight-through MC emulsification for Tween20-containing system does not cause wetting of the channel surface by an oil droplet. The above results demonstrated that a nonionic surfactant (Tween20) is also available for the stable formation of monodisperse oil droplets in straight-through MC emulsification. With an increase in the dispersed phase flux, the

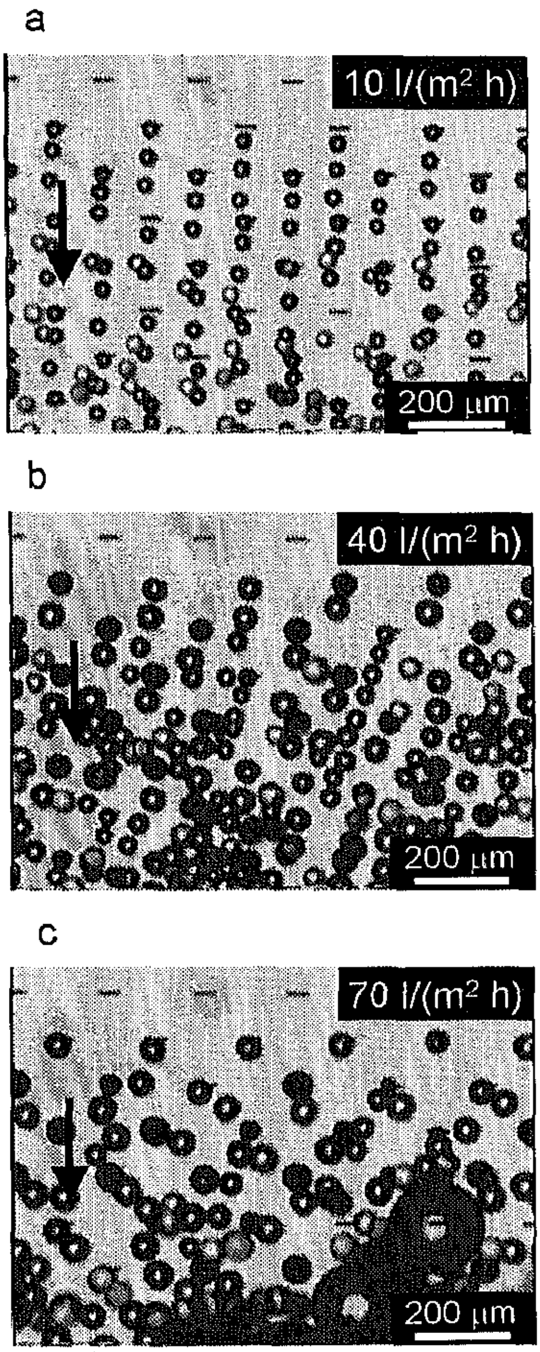

Fig. 6.2.1 Effect of dispersed phase flux for soybean oil/(1.0 wt.% Tween20) water system. (a) Size-stable zone; (b)size-expanding zone 1; (c) size-expanding zone 2. A dispersed phase flux of 40 l/(m^2 h) corresponds to a droplet formation volume rate of 4.0 ml/h per plate.

Tween20-containing system exhibited a size-stable zone (Fig. 6.2.1a), size-expanding zone 1 (Fig. 6.2.1b), and size-expanding zone 2 (Fig. 6.2.1c). The average size and coefficients of variation of the formed oil droplets are shown in Fig. 6.2.2.

Straight-through MC emulsification using cationic surfactants

Straight-through MC emulsification was also conducted using cationic surfactants (CTAB and TOMAC). Figure 6.2.3 shows the straight-through MC emulsification behavior using the CTAB-containing system. Oil droplets that passed through the channels initiated droplet growth with partial wetting on the channel surface (Fig. 6.2.3a). This droplet growth continued until the adjacent droplets were in contact each other, and then their further growth was hindered (Fig. 6.2.3b). The continuous phase flow-driven droplet detachment, as shown in Fig. 6.2.3c, started when the diameters of the oil droplets reached over 100 μm. While they are carried away from the channel surface by the continuous phase flow, shearing of their tails connected to the dispersed phase in the channels for several seconds during the droplet detachment process. This droplet detachment time was much longer than those in the other experimental systems, which are usually less than 0.02 s. Disruption of the tail of the oil droplets completes the droplet formation process, making satellites with diameters below 20 μm (Fig. 6.2.3d). The oil droplets formed from the oblong straight-through MC in CTAB-containing systems exhibited considerable polydispersity. The CTAB-containing system also performed continuous phase flow-driven droplet detachment from the channels at a lower dispersed phase flux of 2.5 $l/(m^2\ h)$ (data are not shown). The preceded phenomena were discussed as follows. There is the affinity between the positively charged group of CTAB and the negatively charged channel surface. In contrast, the CTAB-containing system has a high contact angle of 134°. We consider that these resulted in partial wetting of the oil droplets on the channel surface without spreading on the channel surface. The partial wetting of the oil droplets on the channel in CTAB-containing system would have caused

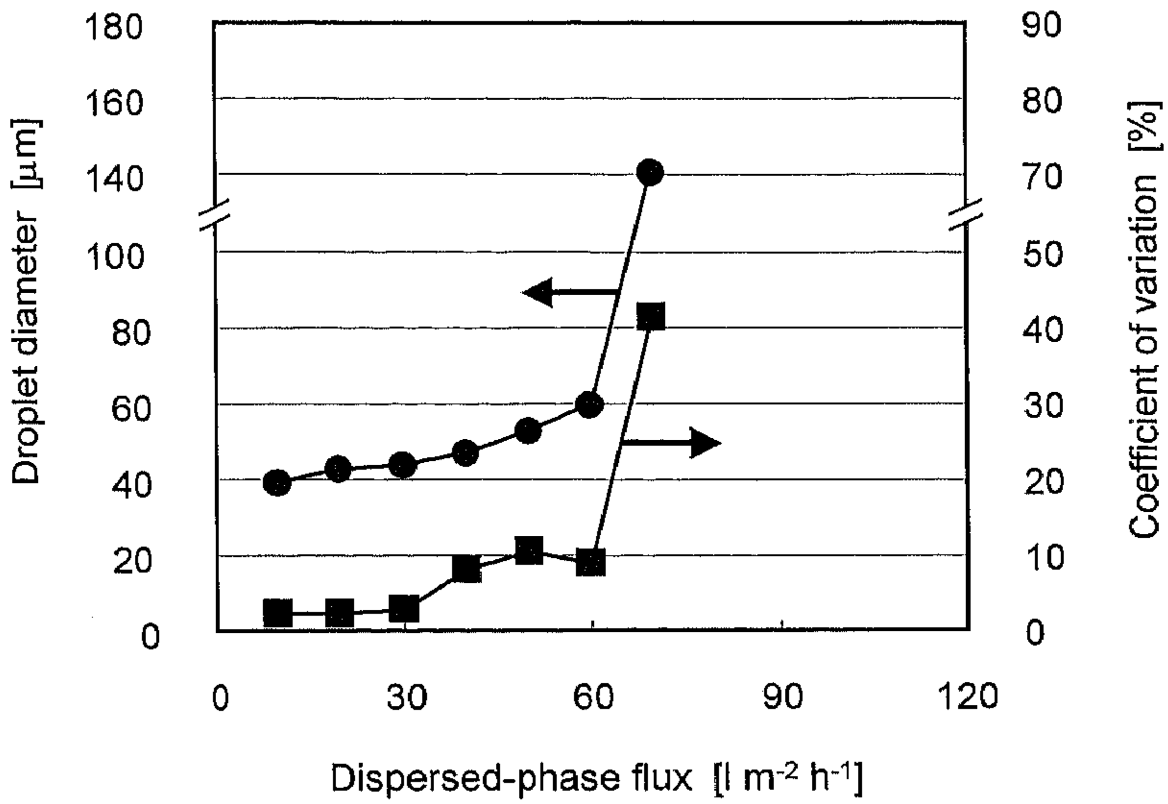

Fig. 6.2.2 Effect of dispersed phase flux on average diameter and coefficient of variation of droplets formed using TMC-B for soybean oil/1.0 wt.% Tween20 aqueous solution system. A dispersed phase flux of 30 l/(m^2 h) corresponds to a droplet formation volume rate of 3.0 ml/h per plate.

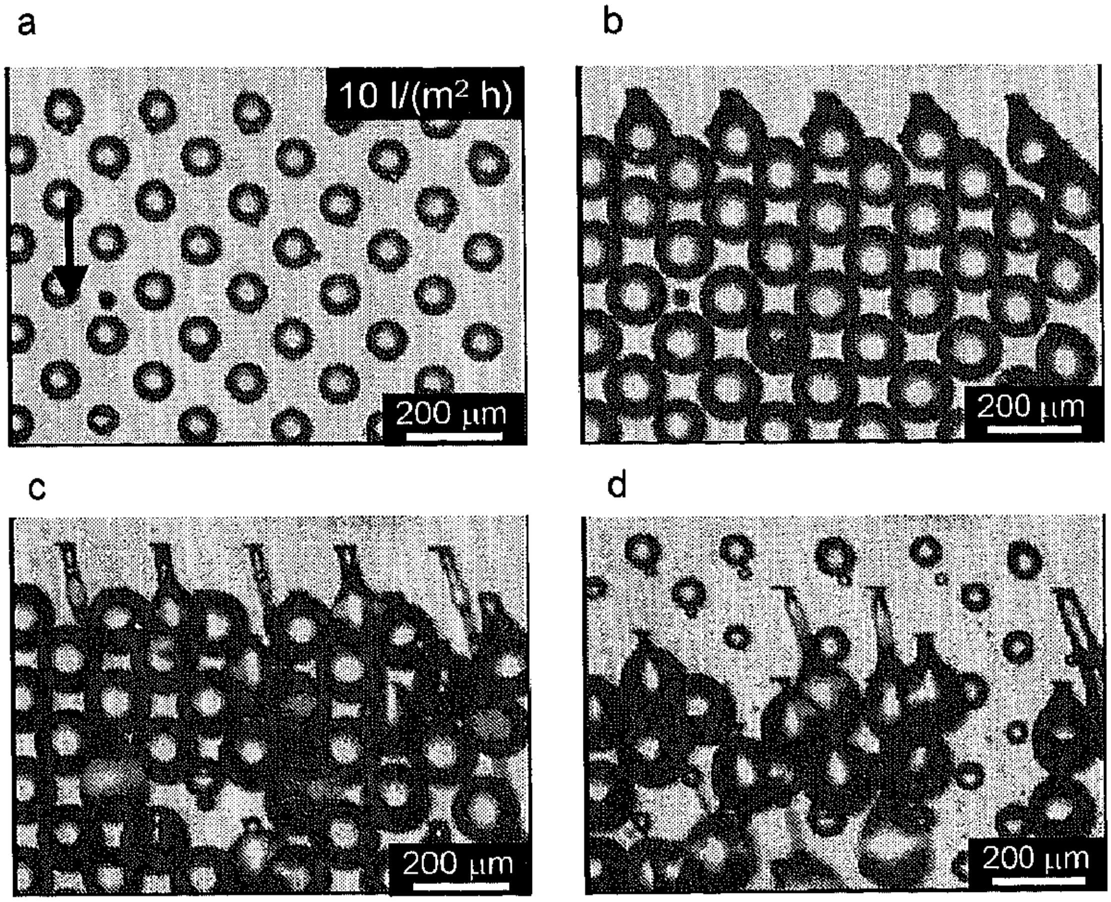

Fig. 6.2.3 Microscopic photographs of droplet formation from an oblong straight-through MC for soybean/(1.0 wt.% CTAB) water system. (a)-(d) Continuous phase flow-driven droplet formation.

the continuous droplet growth and continuous phase flow-driven droplet detachment from the channels. Small interfacial tension of the CTAB-containing system (Table 6.2.1) is the primary reason that the droplets carried away from the channels with creating their tail. Figure 6.2.4 shows the straight-through MC emulsification behavior using the TOMAC-containing system. The dispersed phase that broke through some channels spread smoothly on the channel surface and completely replaced the continuous phase, similarly like the microchannel emulsification behavior using TOMAC (Tong *et al.*, 2000). The strong affinity between the positively charged group of TOMAC and the negatively charged membrane surface promotes its adsorption on the channel surface. The low contact angle of 38° for the TOMAC-containing system also indicates complete wetting of the dispersed phase on the channel surface. As a result, there was a difficulty in forming monodisperse oil droplets by straight-through MC emulsification with the cationic surfactants.

6.2.4 Conclusions

In Chapter 6.2, we have demonstrated that the surfactant charge is a dominant parameter that greatly influences the straight-through MC emulsification behavior. The anionic and nonionic surfactants used were appropriate for stable formation of monodisperse oil droplets from the oblong straight-through MC. In particular, successful straight-through MC emulsification in a nonionic surfactant-containing system is an important result for future applications of straight-through MC emulsification to foods and pharmaceuticals. The resultant monodisperse oil droplets had the average diameters and coefficients of variation of about 40 μm and below 3%, respectively. The repulsive surfactant-channel surface interaction contributed to maintaining the hydrophilicity of the channel surface, which is a prerequisite for stable straight-through MC emulsification. On the other hand, in cationic surfactant-containing systems, we observed formation of polydisperse oil droplets driven by continuous phase flow for CTAB and complete wetting of the dispersed

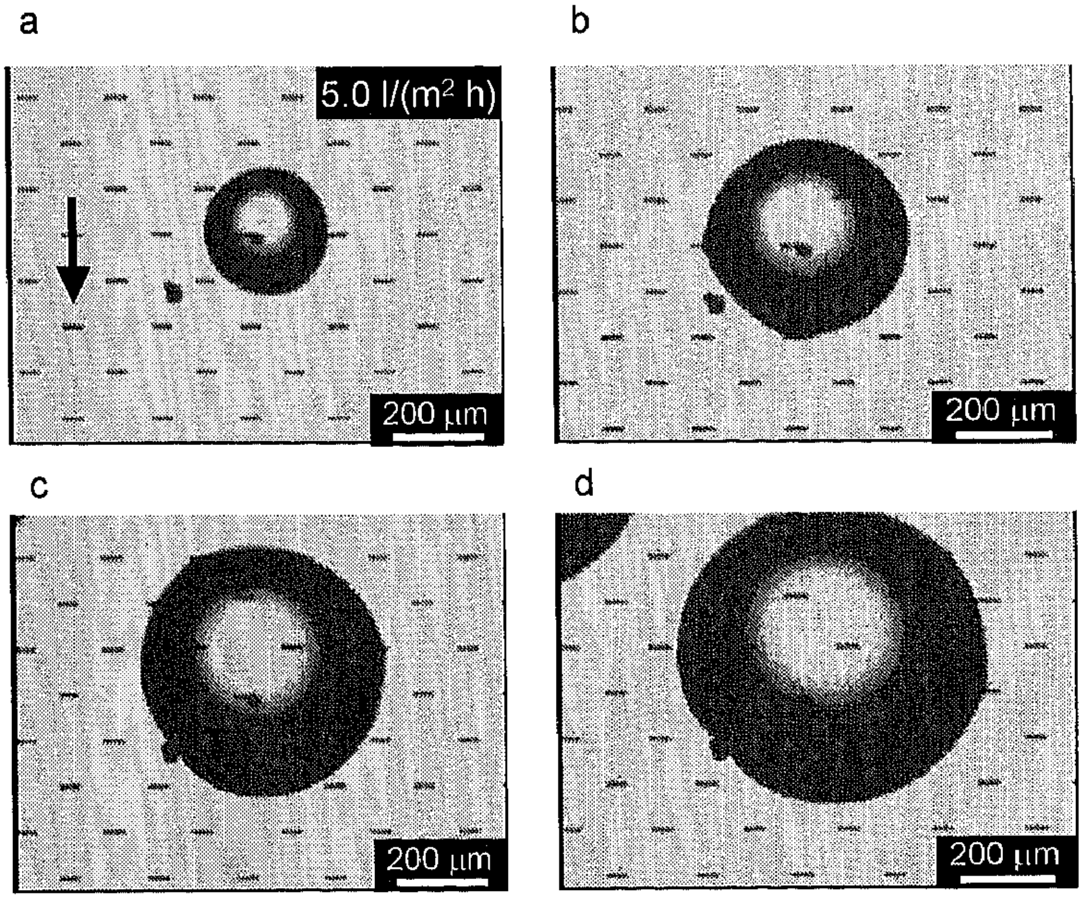

Fig. 6.2.4 Microscopic photographs of wetting of the dispersed oil phase on a channel surface for a soybean oil (2.0 wt.% TOMAC)/water system.

phase on the channel surface for TOMAC. The strong surfactant-channel surface affinity in the systems led to unsuccessful straight-through MC emulsification.

6.3 Effect of Food-Grade Surfactants on Preparation of Soybean Oil-in-Water Emulsions in Straight-Through Microchannel Emulsification

6.3.1 Introduction

Emulsions composed of biocompatible ingredients form the basis of a wide variety of foods, pharmaceuticals and cosmetics (McClements, 1999; Buszello and Müller, 2000). Many of their physicochemical and organoleptic properties are determined by the droplet size and size distribution of emulsions (McClements, 1999). Surfactants available for producing food and pharmaceutical emulsions are restricted in type and amount. They are nonionic surfactants except for phospholipids, which are amphilic surfactants. Thus, food and pharmaceutical emulsions are commonly prepared using mechanical emulsification devices such as despersing machines, rotor/stator systems, and high-pressure homogenizers (McClements, 1999; Karbstain and Schubert, 1995).

Recently developed emulsification devices for the preparation of monodisperse emulsions, membrane emulsification (Nakashima *et al.*, 1991) and microchannel (MC) emulsification (Kawakatsu *et al.*, 1997), require smaller shear stress and lower energy input to prepare emulsions than conventional devices (Schröder *et al.*, 1998). These features can develop new products with shear-sensitive ingredients (Schröder *et al.*, 1999). Emulsions prepared by membrane emulsification have applications in foods and pharmaceuticals, such as low-fat spread (Katoh *et al.*, 1996), multiple drug emulsions (Higashi *et al.*, 1995), and microcapsules (Muramatsu and Kondo, 1995). MC emulsification has also been prepared monodisperse lipid microparticles (Sugiura *et al.*, 2000) and phospholipid emulsions (Tong *et al.*, 2002) for food and pharmaceutical use.

In chapter 6.2, we demonstrated that it is possible to stably form monodisperse oil droplets in straight-through MC emulsification using a nonionic surfactant with a marked ability to prepare an oil-in-water (O/W) emulsion. In Chapter 6.3, the formation characteristics of food-grade soybean oil-in-water emulsion droplets using different food additive grade surfactants by straight-through MC emulsification were studied. The preparation characteristics of monodisperse O/W emulsions using selected food-grade surfactants were also described.

6.3.2 Materials and Methods

Materials

Refined soybean oil (Wako Pure Chemical Ind., Osaka, Japan) was used as the dispersed phase. The soybean oil used has a saponification value of 190, an iodine value of 130, an acid value below 0.2 and phospholipid content below 10 mg/kg, respectively (Catalogue value). MilliQ water (Millipore Co., Massachusetts, USA) was used to prepare all of the continuous phase solutions. Pentaglycerol monolaurate [PGM, 65% purity; Sun soft A-121E; hydrophilic lipophilic balance (HLB), 12] (Taiyo Kagaku Co., Ltd., Mie, Japan), polyoxyethelene (20) sorbitan monolaurate [Tween20; HLB, 15] (Wako Pure Chemical Ind., Osaka, Japan), and sucrose monostearate [SE, >70% purity; SS; HLB, 19] (Dai-ichi Kogyo Seiyaku Co., Ltd., Tokyo, Japan) were used as the food additive grade surfactants.

Experimental setup

The straight-through silicon MC plate used in Chapter 6.3 was described in detail in Chapter 6.1.2. Two types of oblong straight-through MCs (TMC-A5 and TMC-B) were used in Chapter 6.3. The dimensions of the straight-through MCs are presented in Table 6.3.1. TMC-A5 was employed for screening food-grade surfactants suitable for forming monodisperse emulsion droplets, and TMC-B for preparing monodisperse emulsions using selected food-grade surfactants. Details of the straight-through MC emulsification system were described in Chapter 5.2.

Straight-through MC emulsification

All of the continuous phase fluids were prepared by dissolving each food-grade surfactant into water at a concentration higher than the critical micelle concentration (CMC). The straight-through MC emulsification procedures were described in detail in Chapter 6.1.

Table 6.3.1 Dimensions of silicon straight-through MC plates used.

Channel type	Channel equivalent diameter[a] (μm)	Longer channel length L (μm)	Shorter channel length S (μm)
TMC-1	22.1	52.5	14.0
TMC-2	16.0	48.7	9.6

[a]Channel equivalent diameter is defined as four times the cross-sectional area divided by the wetted perimeter of the channel.

Measurements and analysis

Video images taken during the experimental runs were analyzed to understand the droplet formation from the straight-through MC. Droplet size measurements were conducted by the method described in Chapter 5.2. The average droplet diameter and coefficient of variation of the prepared emulsions were calculated from the measured droplet diameters. The coefficient of variation, which provides the degree of the droplet size distribution, was described in detail in Chapter 2.2.

Interfacial tension measurement method was described in detail in Chapter 2.2. The contact angle of an oil droplet to the channel surface in the continuous phase was also determined from the photograph of an oil droplet in contact with the channel surface.

6.3.3 Results and Discussion

Effect of food-grade surfactant type

The effect of the food-grade surfactant on oil droplet formation from an oblong straight-through MC was investigated. Food-grade surfactants (PGM, Tween20, and SE) with a marked ability to prepare O/W emulsions were used at a concentration of 1 wt% in the continuous phase. TMC-A5 was employed as the straight-through MC. The PGM- and Tween20-containing systems exhibited successful straight-through MC emulsification (Fig. 6.3.1a); uniformly sized O/W emulsion droplets were stably formed from the straight-through MC. There was neither the formation of irregularly sized large droplets and or a continuous growth of the dispersed phase, which could result in a broad size distribution. Figure 6.3.2 shows the droplet diameter distribution of the resultant O/W emulsions. Their average droplet diameter and coefficient of variation were 49.0 μm and 1.4% for PGM (Fig. 6.3.2a) and 48.9 μm and 2.1% for Tween20 (Fig. 6.3.2b). The microscopic photograph in Fig. 6.3.1b also confirms their excellent monodispersity. It is generally difficult to form monodisperse emulsion droplets with diameters of 50 μm by conventional emulsification techniques. Successful straight-through MC emulsification for PGM and Tween20 was performed even without the continuous phase

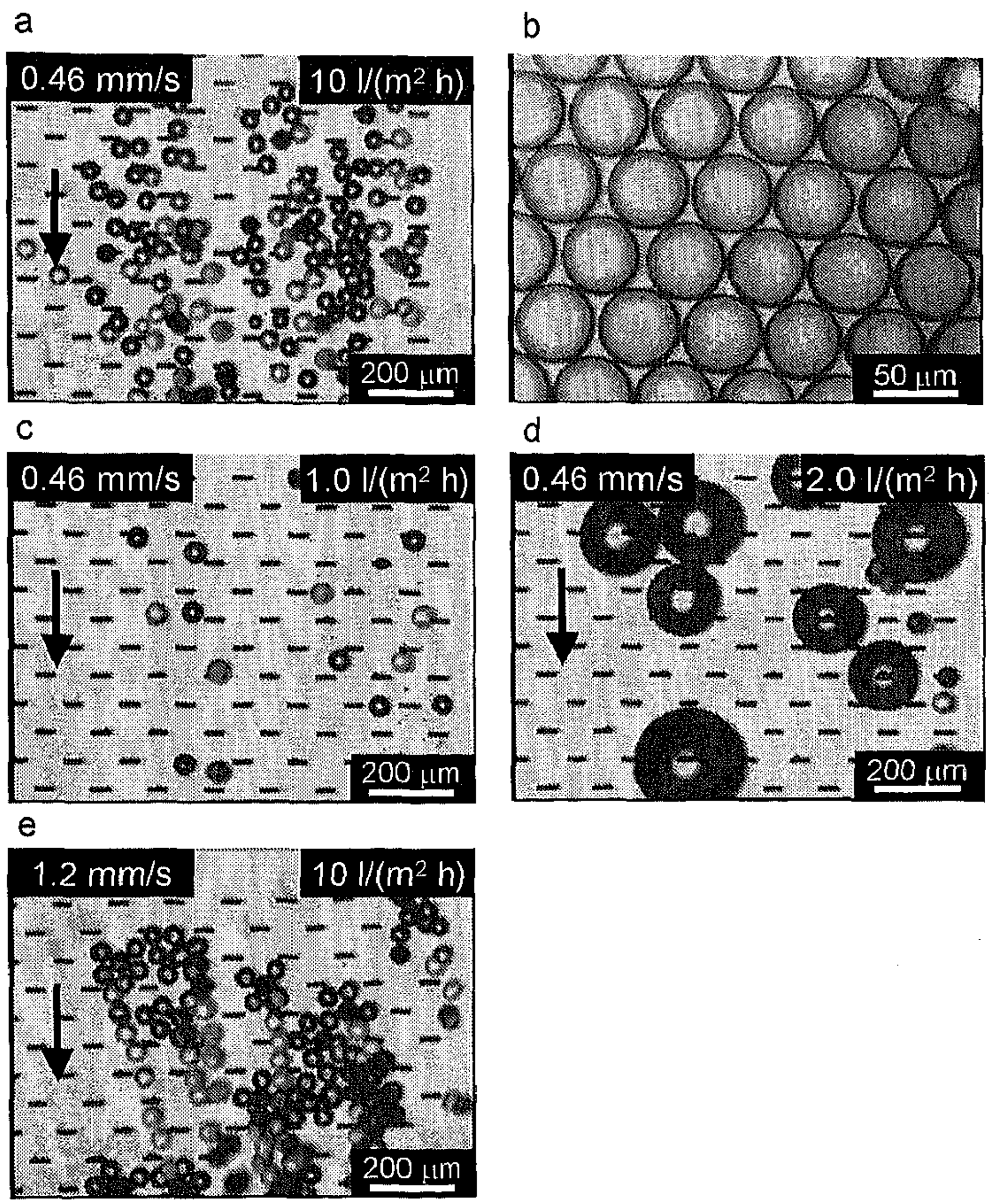

Fig. 6.3.1 Microscopic photographs of the straight-through MC emulsification process using TMC-1. (a), (b) Droplet formation and formed monodisperse O/W emulsion droplets for a soybean oil/water (1.0 wt.% PGM) system; (c), (d) droplet formation for a soybean oil/water (1.0 wt.% SE) system; (e) dropletformation for a soybean oil/water system. A dispersed phase flux of 10 l/(m^2 h) corresponds to a droplet formation volume rate of 1.0 ml/h per plate.

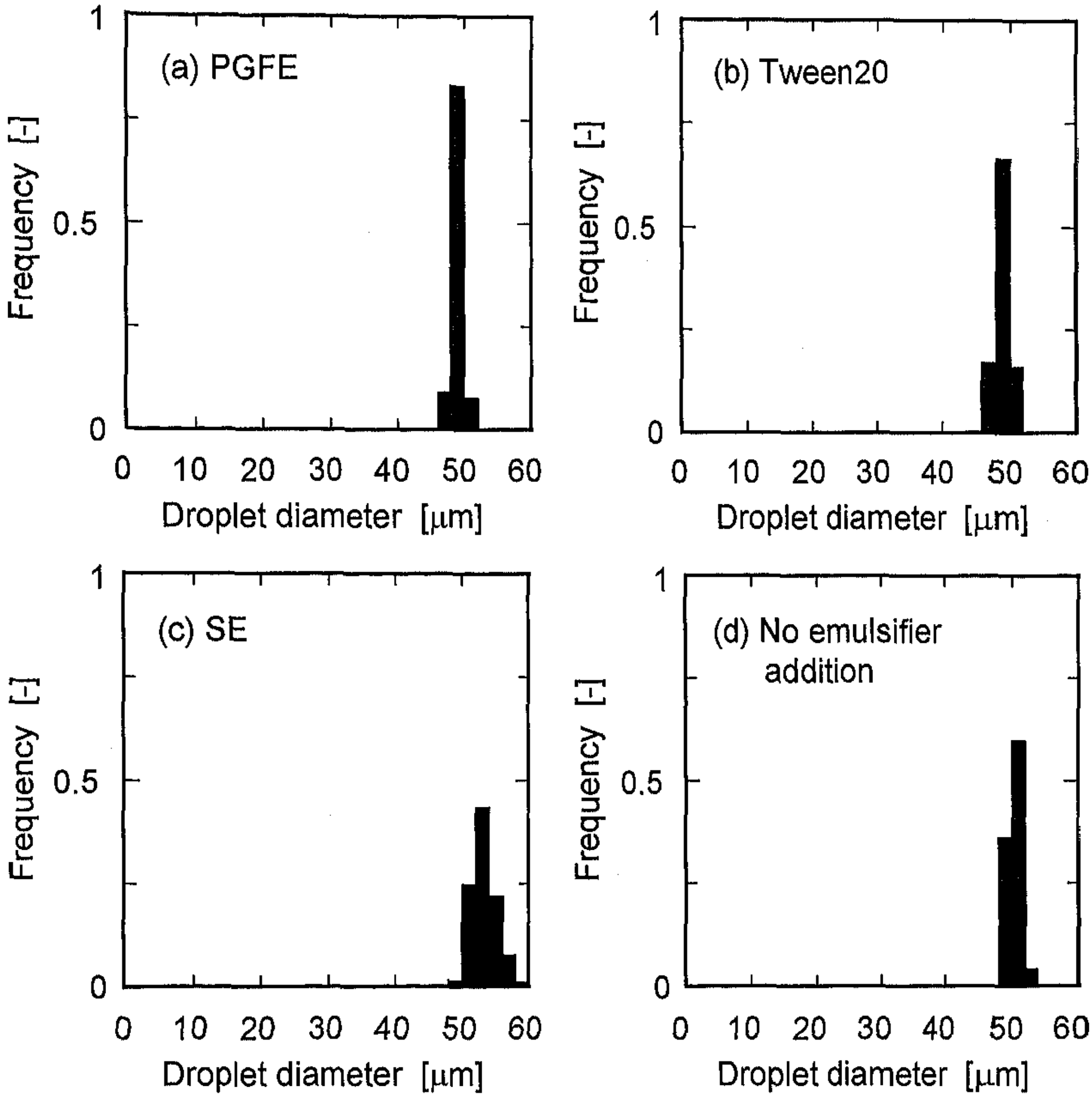

Fig. 6.3.2 Droplet diameter distribution for soybean oil-in-water emulsion droplets.

flow, which suggests spontaneous formation of monodisperse emulsion droplets from the oblong straight-through MC (see Chapter 5.4). There was little change in the average diameter and coefficient of variation of the resultant emulsion droplets over the applied continuous-phase flow velocities. Straight-through MC emulsification that can form monodisperse emulsion droplets in a gentle continuous phase flow is advantageous for preparing food and pharmaceutical emulsions containing shear-sensitive ingredients. The above results demonstrate that PGM and Tween20 are potential food-grade surfactants to stably prepare monodisperse O/W emulsions by straight-through MC emulsification.

Figures 6.3.1c and d depict microscopic photographs of the straight-through MC emulsification process for SE. We first applied a dispersed phase flux of 10 l/(m^2 h) (a droplet formation volume rate of 1.0 ml/h per plate) in a similar manner as in the experimental systems described above. However, the dispersed phase droplets that broke through the straight-through MC continued to grow to 150 μm or more at the channel tip, and then the neighboring droplets, which were in contact, were forced to detach from the channel tip. Straight-through MC emulsification was next conducted at a lower dispersed phase flux of 1.0 l/(m^2 h) to investigate the effect of the dispersed phase flux on the straight-through MC emulsification behavior for SE. The SE-containing system yielded monodisperse O/W emulsion droplets from the straight-through MC at a dispersed phase flux of 1.0 l/(m^2 h), as illustrated in Fig. 6.3.1c. They had an average droplet diameter of 53.2 μm and a coefficient of variation of 3.3% (Fig. 6.3.2c), which indicates that their droplet size was slightly larger than those for PGM and Tween20. The dispersed phase flux was then increased in steps. The dispersed phase that broke through the straight-through MC recommenced growing continuously at a dispersed phase flux of 2.0 l/(m^2 h) or more (Fig. 6.3.1d). However, no wetting of the dispersed phase at the channel tip was observed over the applied dispersed phase flux. The straight-through MC emulsification behavior for SE is discussed below. The SE-containing system thus achieved successful straight-through MC emulsification in a considerably narrow range of dispersed phase flux, lower than 1.0 l/(m^2 h).

Straight-through MC emulsification was also conducted using a soybean oil/water system without the addition of surfactant. We applied a continuous-phase flow velocity of 1.2 mm/s to avoid contact between the resultant emulsion droplets, considering their instability against coalescence. Uniformly sized O/W emulsion droplets were formed from the straight-through MC at a dispersed phase flux of 10 l/(m^2 h) in this case (Fig. 6.3.1e). The emulsion droplets that resulted just after formation had an average droplet diameter of 50.3 μm and a coefficient of variation of 1.9% (Fig. 6.3.2d). MC emulsification using an experimental system without the addition of surfactant also formed uniformly sized emulsion droplets (Sugiura *et al.*, 2000). Although several emulsion droplets adhered to the plate surface close to each of the droplets-forming channel, they did not spread on the plate surface (Fig. 6.3.1e). The above results clarify that it is possible to spontaneously form uniformly sized emulsion droplets in straight-through MC emulsification.

Analysis of straight-through MC emulsification

The effect of the food-grade surfactants on the straight-through MC emulsification behavior is discussed based on the results obtained in Chapter 6.3. One prerequisite for preparing monodisperse emulsions by membrane emulsification (Nakashima *et al.*, 1991, 2000) and MC emulsification (Tong *et al.*, 2000) is to prevent the membrane and channel surfaces from wetting by the dispersed phase. The wetting properties of the channel surface with the dispersed phase have been evaluated using the contact angle (Tong *et al.*, 2000; Kawakatsu *et al.*, 2001). The measured contact angle data for experimental systems using different food-grade surfactants are presented in Table 6.3.2. The experimental systems with surfactants had high contact angles ranging from 142 to 146°, although no strong repulsion existed between the hydrophilic group of nonionic emulsifier molecules and the negatively charged plate surface. These contact angles suggest that the channel surface can remain hydrophilic during the straight-through MC emulsification

Table 6.3.2 Contact angle and interfacial tension of the experimental systems used.

Emulsifier[a]	Condition	Contact angle[b] (deg)	Interfacial tension (mN/m)
PGFE	1.0 wt% (W)[c]	143	4.4
Tween20	1.0 wt% (W)	142	1.9
SE	1.0 wt% (W)	145	1.4
None	-	130	23.4

[a]PGFE, polyglycerol fatty acid ester; Tween20, polyoxyetylene (20) monolaurate; SE, sucrose monostearate.

[b]Contact angle between an oil droplet and the channel surface in the water phase.

[c]Dissolved in the continuous water phase.

process. Moreover, the measured interfacial tensions (Tab 6.3.2) demonstrated proper interfacial activity for the food-grade surfactants used. Successful straight-through MC emulsification for PGM- and Tween20-containing systems can be explained by the above factors.

The experimental system without the addition of surfactant also had a high contact angle of 130°, which was slightly lower than the other experimental systems with surfactants. This contact angle supports the belief that this experimental system is still capable of forming uniformly sized droplets from the straight-through MC. The high contact angle data for this experimental system also verifies the result in Fig. 6-3-1e in that the adhering emulsion droplets did not spread on the plate surface.

The SE-containing system exhibited an insignificant difference in the measured contact angle and interfacial tension compared to PGM- and Tween20-containing systems (Table 6.3.2), satisfying the conditions necessary for performing successful straight-through MC emulsification. However, monodisperse emulsion droplets were formed from the straight-through MC only at a considerably low dispersed phase flux, below 1.0 l/(m^2 h), for the SE-containing system, as depicted in Figs. 6.3.1c and d. The experimental system without the addition of surfactant exhibited stable droplet formation from the straight-through MC at a dispersed phase flux of 10 l/(m^2 h) (Fig. 6.3.1e). Adsorption of SE molecules at an oil/water interface apparently cause unstable droplet formation from a straight-through MC. The surfactant adsorption at an oil-water interface affects the interfacial rheological characteristics (Rodríguez *et al.*, 2001). The SE used has a melting point (52°C) much higher than those of PGM and Tween20. It must be noted that emulsifier crystallization did not occur in the 1.0 wt.% SE aqueous bulk solution used as the continuous phase. SE molecules gradually accumulated at the oil-water interface during droplet growth from the straight-through MC. We therefore assumed that the accumulation of SE molecules in this region would cause their interfacial crystallization. The interfacial crystallization characteristics of food-grade surfactants (monoglycerol fatty acid esters) with high-melting points at the oil-water interface were reported previously (Rodríguez *et al.*, 2001). We believe that the interfacial crystallization of SE molecules may make lower the mobility of an interfacial layer. The elongated oil/water interface at the channel tip in straight-through MC emulsification must be spontaneously sheared to form monodisperse droplets. Sugiura *et al.* (2001) proposed a spontaneous shearing mechanism of the elongated oil/water interface, which passed through a grooved MC with an elongated section. The SE-adsorbed interfacial layer may make it more difficult to be sheared due to its low mobility. This would explain why continuous growth of dispersed phase droplets from the straight-through MC took place, even at a low dispersed phase flux of 2.0 l/(m^2 h) for the SE-containing system. Therefore, the interfacial rheological characteristics should also be considered to stably form monodisperse emulsion droplets from a straight-through MC.

Preparation of monodisperse food-grade O/W emulsions

The food-grade surfactants used were PGM and Tween20, which resulted in successful straight-through MC emulsification. TMC-B was employed as the straight-through MC. The dispersed phase volume fraction of the resulting emulsions was controlled at 2% during the straight-through MC emulsification process. Figure 6.3.3a shows a microscopic photograph of the straight-through MC emulsification process for PGM. Optical observations of this straight-through MC emulsification revealed that all the channels working in TMC-B yielded monodisperse O/W emulsion droplets. Figures 6.3.4a and c depict the droplet diameter distribution of the emulsion droplets just after droplet formation for PGM and Tween20. Their average diameter and coefficient of variation were 38.9 μm and 2.3% for PGM and 38.1 μm and 1.9% for Tween20, which indicates that TMC-B is applicable to the preparation of monodisperse O/W emulsions. We subsequently recovered the emulsion droplets formed using TMC-B. The recovered emulsions rapidly formed a concentrated cream layer; no bulk oil phase appeared and the cream layer was easily dispersed by shaking. The effect of the recovery process of the

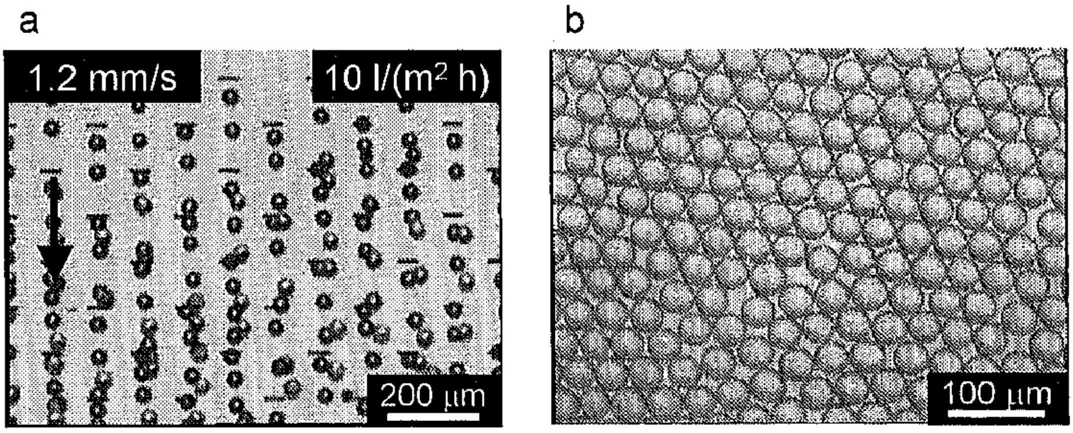

Fig. 6.3.3 Microscopic photographs of the straight-through MC emulsification process using TMC-2. (a), (b) Droplet formation and recovered monodisperse O/W emulsion droplets for a soybean oil/water (1.0 wt.% PGM) system.

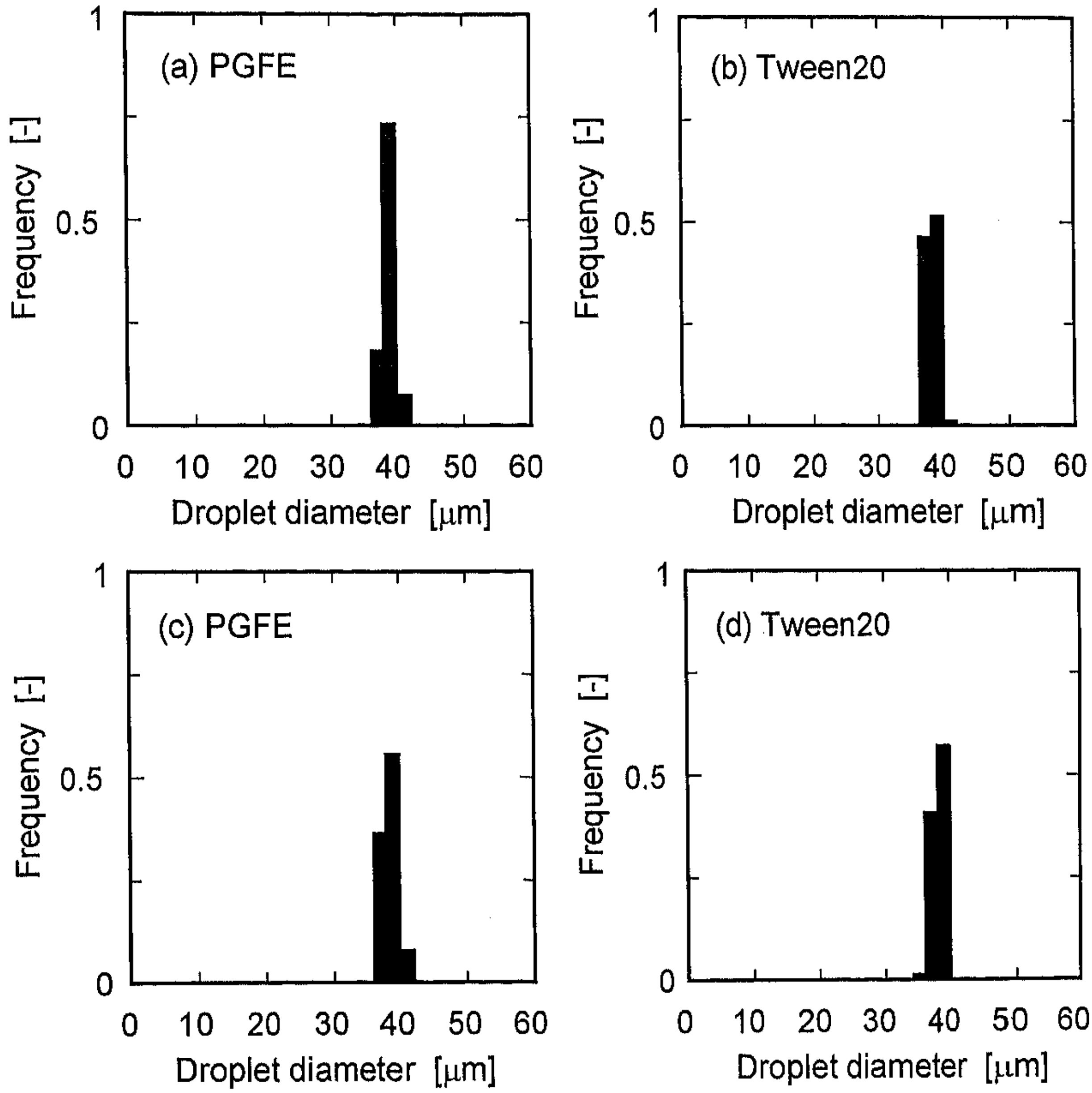

Fig. 6.3.4 Droplet diameter distribution for soybean oil-in-water emulsion droplets. (a), (b) O/W emulsion droplets just after formation; (c), (d) O/W emulsion droplets after recovery.

formed emulsion droplets on their size and size distribution was also evaluated. Figures 6.3.4b and d show the droplet diameter distribution of the recovered emulsions for PGM and Tween20. Their average droplet diameter and coefficient of variation were 38.6 μm and 2.6% for PGM and 37.9 μm and 2.0% for Tween20. The microscopic photograph of the recovered emulsion droplets for PGM (Fig. 6.3.3b) also verified their monodispersity. This result suggests that the recovery process of the formed emulsion droplets did not cause droplet coalescence during the process. We can conclude that straight-through MC emulsification using suitable food-grade surfactants yields superior performance in the preparation of monodisperse food-grade O/W emulsions.

6.3.4 Conclusions

In Chapter 6.3, we have shown that monodisperse food-grade soybean oil in water emulsion droplets were stably formed by straight-through MC emulsification using suitable food-grade surfactants, such as PGM and Tween20. The O/W emulsion droplets formed using TMC-A5 for PGM and Tween20 had average droplet diameters of 49 μm and coefficients of variation below 3%. In contrast, the SE-containing system resulted in unstable droplet formation at a low dispersed phase flux of 2.0 $l/(m^2$ h). There were insignificant differences in the measured contact angles and interfacial tensions among all of the experimental systems with food-grade surfactants. An analysis of the surfactant adsorbed oil/water interfacial layer confirmed that the interfacial rheological properties must also be considered in straight-through MC emulsification. Monodisperse food-grade emulsions with average droplet diameters of 38 to 39 μm and coefficients of variation below 3% were successfully prepared using TMC-B with the selected food-grade surfactants (PGM and Tween20). Thus, straight-through MC emulsification can be used to prepare monodisperse food-grade O/W emulsions.