

Characterization of Spontaneous Transformation-Based Droplet Formation during Microchannel Emulsification

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Recently, we proposed a microchannel (MC) emulsification technique, which is a novel method for making a monodispersed emulsion from a microfabricated channel array. The droplet formation mechanism for MC emulsification is a unique one, in which the distorted dispersed phase is spontaneously transformed into spherical droplets by interfacial tension. The objective of this study was to characterize the flow in MC emulsification. We investigated the emulsification behavior at different flow velocities of the dispersed phase using MCs with different sizes and analogous shapes and found a critical flow velocity over which the character of flow changed drastically. The formed droplet diameters were almost constant below the critical velocity, and monodispersed emulsions were formed. The droplet diameters increased drastically above the critical velocity, and polydispersed emulsions were formed. The critical velocities were independent of MC size. Analysis using a dimensionless number revealed that the critical point, at which the character of the flow of MC emulsification changes, is determined by the Capillary number (Ca), which is the ratio of viscous force to interfacial tension force. Below the critical Ca , the interfacial tension, which is the driving force for droplet formation, is dominant, and the flow in MC emulsification was based on spontaneous transformation. Above the critical Ca , viscous force is dominant, and the flow is similar to laminar flow. We experimentally confirmed this idea using the dispersed and continuous phases with different viscosities, MCs with different sizes, and different interfacial tensions. These results suggested a law of similarity in MC emulsification, and the transition of the flow was determined by Ca . The information obtained in this study includes the essential physics underlying spontaneous transformation flow in MC emulsification and is useful for practical applications.

1. Introduction

Emulsions have been utilized in various industries, including food, cosmetics and pharmaceutical industries. Many of the most important properties of emulsion-based products (e.g., shelf life, appearance, texture, and flavor) are determined by the size of the droplets they contain.¹ The stability, rheology, appearance, chemical reactivity, and physical properties depend on their droplet size and size distribution.^{1–3} Resistance to creaming and Ostwald ripening of emulsions are influenced by their size and size distribution.^{2,3} Furthermore, colloidal interactions between emulsion droplets are affected by the droplet size. Consequently, it is important to reliably predict and control the emulsion size and size distribution.

Monodispersed emulsions are useful for fundamental studies because the interpretation of experimental results is much simpler than for polydispersed emulsions.² They can also serve as useful systems for measuring important properties of emulsions. For example, the stability of droplets can be monitored very simply because changes in the droplet size are easily studied by having monodispersed droplets. Monodispersed emulsions can greatly reduce Ostwald ripening by reducing the

effective Laplace pressure difference because the droplets are identical in size. The effects of change in the droplet size on physical properties of emulsions can be studied directly. Monodispersed emulsions are also useful for practical applications of valuable materials, such as microcapsules for drug delivery vehicles^{4–6} and monodispersed microparticles.⁷

Several research groups have tried to produce monodispersed emulsions. Membrane emulsification, in which the pressurized dispersed phase permeates a microporous membrane and forms emulsion droplets, enables us to produce monodispersed emulsions with a coefficient of variation of approximately 10%.^{8–10} The emulsion droplet size is controlled by the membrane pore size. This technique can be used to produce emulsions without strong mechanical stress.¹¹ Mason and Bibette proposed that the shear rupturing in Couette flow can be applied to produce monodispersed emulsions.^{12–14}

Recently, we proposed a novel method for making monodispersed emulsion droplets from a microfabricated channel array.¹⁵ This emulsification technique is called microchannel (MC) emulsification. Emulsions with a coefficient of variation of approximately 5%¹⁶ and droplet sizes of 3 to 100 μm have been successfully prepared by applying this technique.^{17,18} The droplet diameter was determined by the geometry of MC.^{19,20} This technique is promising not only for preparing emulsions but also for a variety of systems. We have applied it to preparing several types of oil-in-water emulsions,²¹ water-in-oil emul-

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sions,²² lipid microparticles,²³ polymer microparticles,²⁴ and microcapsules. Monodispersed emulsions prepared by MC emulsification have also been used for fundamental studies.²⁵ Using the present system, the production rate of emulsion is 1–10 mL/h in the case of 10% of the volume fraction. For scale-up of the equipment, the through-type systems have been proposed, on which 10 000 of the through-type MCs were fabricated on one plate.²⁶ Further scale-up may be possible using the MC plate with large surface area and accumulation of the MC plate.

MC emulsification exploits the interfacial tension, which is the dominating force on a micrometer scale, as the driving force for droplet formation. The MC structure is composed of a narrow channel part and a slitlike terrace part. During droplet formation, the distorted dispersed phase is spontaneously transformed into spherical droplets by interfacial tension.¹⁶ The mechanism is similar to the elongational transformation in the point that transformation is driven by interfacial tension.²⁷ The energy input for MC emulsification is very low compared to the conventional emulsification technique because droplet formation from an MC is based on spontaneous transformation.¹⁶

This droplet formation process caused by spontaneous transformation is a hydrodynamic process. An analysis of the droplet formation process should involve the solution of the Navier–Stokes equation, along with the proper boundary conditions. However, mathematical complexities of the equation, considering the intricately shaped interface and wetting phenomena, preclude this approach. As an alternative, we employed analysis using dimensionless numbers in this study to characterize the flow of droplet formation in MC emulsification. The emulsification behavior at different flow velocities of the dispersed phase was investigated using MCs with different sizes and analogous shapes and using the dispersed and continuous phases with different viscosities but the same viscosity ratio. The forces affecting the emulsification behavior are discussed through the analysis using dimensionless numbers.

2. Materials and Methods

2.1. Materials. Triolein (purity >90%) was obtained from Nippon Lever B. V. (Tokyo, Japan). Castor oil was obtained from Wako Pure Chemical Ind. (Osaka, Japan). Triolein was used as the dispersed oil phase, and its viscosity was controlled by mixing with castor oil. MilliQ water was used as the continuous water phase. Sodium dodecyl sulfate (SDS) was purchased from Wako Pure Chemical Ind. and used as the surfactant for emulsification. Polyethylenglycole (PEG) was obtained from Wako Pure Chemical Ind. and used to control the viscosities of the continuous phases.

2.2. Measurement and Analytical Method. The droplet diameter was determined from pictures obtained with the microscope. Winroof (Mitani Corporation, Fukui, Japan) software was used to analyze the captured pictures. The interfacial tension was measured using a Full automatic interfacial tensiometer (PD-W; Kyowa Interface Science Co., Ltd., Saitama, Japan). The viscosities of both phases were measured with a microviscometer (HAAKE, Karlsruhe, Germany). The densities were measured with picnometers.

2.3. MC Emulsification. The laboratory-scale apparatus for preparing monodispersed emulsions consists of a silicon MC plate, a MC module, and liquid chambers supplying continuous and dispersed phases.¹⁵ Figure 1 shows the experimental setup and schematic flow of the dispersed oil phase through the silicon MC. The emulsification behavior was observed through the glass plate using a microscope. In this study, a high-speed camera

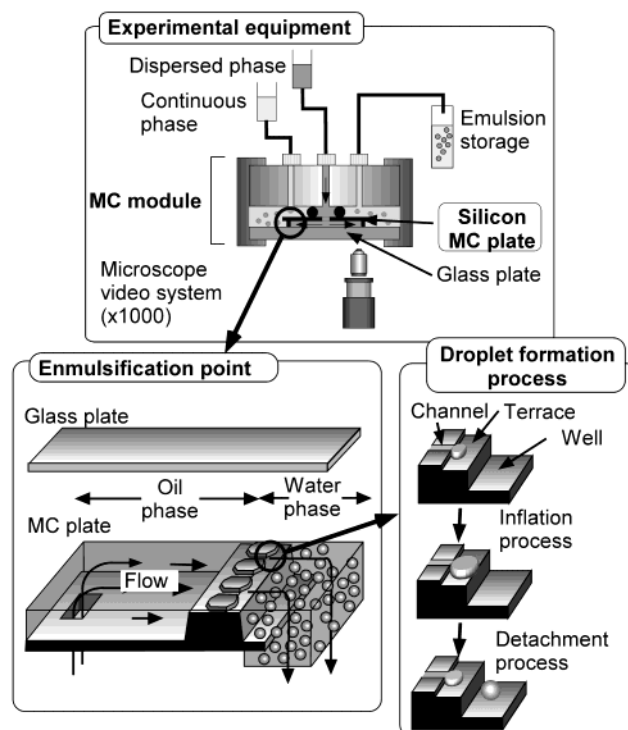


Figure 1. Experimental setup and schematic flow of the dispersed oil phase through the silicon MC.

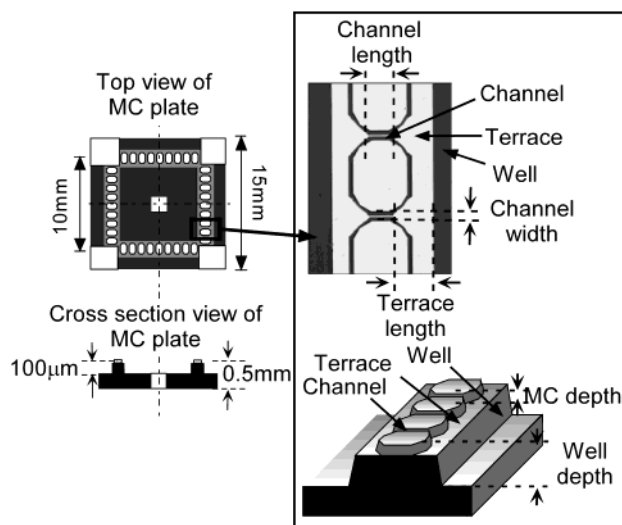


Figure 2. Silicon MC plate used in this study.

(FASTCAM ultima 1024; Photron Ltd., Tokyo, Japan), which can capture 16 000 frames/s, was attached to the microscope to observe the emulsification behavior. Figure 2 shows the schematic of the MC plate used in this study. The silicon MC plate was fabricated using photolithography and orientation-dependent etching.²⁸ The silicon MC plate measured 15 mm × 15 mm, and a 1 mm diameter hole was produced at the center of the plate. Four terrace lines with a height of 100 μm and a length of 10 mm were fabricated on the MC plate. MCs were fabricated on each terrace line. In the present study, MCs with different sizes and analogous shapes were used. The dimensions of the MC plates used in this study are shown in Table 1.

The MC module was initially filled with the continuous phase. The dispersed phase, which was pressurized by the head difference of the liquid chamber, entered the space between the silicon MC plate and the glass plate. The pressurized dispersed

TABLE 1: Dimensions of the MC Plates Used in This Study

MC plate	MC depth [μm]	terrace length [μm]	channel length [μm]	channel width (average) [μm]
MC-2	2	15	7.7	3.3
MC-4	4	28	14	4.7
MC-8	8	57	32	8.3
MC-16	16	113	68	16

phase passes through the channel and inflates on the terrace in a disklike shape (Inflation process). This distorted disklike shape is the essential point for spontaneous transformation because the disklike shape has a greater interface area than the spherical shape, which results in instability from the viewpoint of interface free energy. When the dispersed phase reaches the end of the terrace, it detaches from the terrace and is spontaneously transformed into spherical droplets by interfacial tension (Detachment process). The prepared emulsion was recovered by a continuous phase flow.

3. Results and Discussion

MC emulsification was carried out using MCs with analogous shapes and different sizes. We investigated droplet formation behavior while changing the flow velocity of the dispersed phase through the channel and using triolein as the dispersed oil phase. SDS 1% aqueous solution was used as the continuous phase. The viscosities of the dispersed phase and continuous phase were 60 and 1.1 mPa s, the interfacial tension of the system was 4.5 mN/m, and the MC emulsification was carried out at 25 °C. Droplet diameters and detachment times were measured at the different flow velocities of the dispersed phase using MCs with different sizes. The detachment time is defined as the time from the point that the dispersed phase reaches the terrace end to the time at which the dispersed phase detaches from the MC and forms a spherical droplet (Figure 1). We observed the droplet formation behavior from a single channel at the center of the terrace line and calculated flow velocities of the dispersed phase through the channel from the droplet diameters and droplet formation rates.

Figure 3 shows the droplet diameters and detachment times at different flow velocities of the dispersed phase using different MC sizes. We observed the critical flow velocity for each MC size over which the flow character changed drastically. The formed droplet diameters were almost proportional to the MC size and were almost constant below the critical flow velocity. The droplet diameter significantly increased over the critical velocity. This means that the system should be operated below critical velocity for practical applications. Droplet detachment times were approximately proportional to MC size to the power of $3/2$ and significantly increased above the critical velocity. Interestingly, the critical velocities were independent of MC size.

The experimental observation shows that the character of the flow changed drastically above the critical flow velocity (Figure 4). In other words, the transition of the state of flow in the MC was observed above the critical velocity. Below the critical velocity, the interfacial tension, which is the driving force of droplet formation in MC emulsification, dominates other forces. The state of flow is based on the spontaneous transformation caused by interfacial tension (spontaneous transformation flow), and monodispersed droplets are formed (Figure 4A). Above the critical velocity, the interfacial tension is not dominant, and the dispersed phase flows out continuously (continuous outflow, Figure 4B).

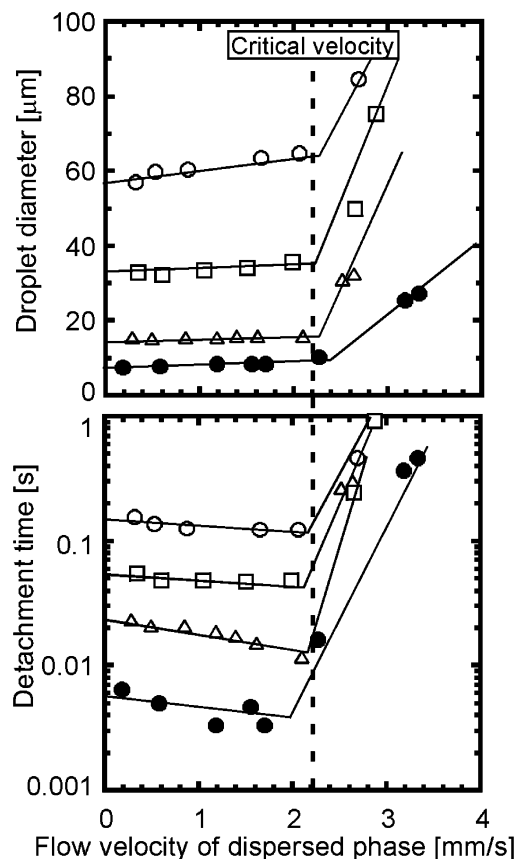


Figure 3. Droplet diameters and detachment times at different flow velocities of the dispersed phase using different MC sizes. MC depths are 16 (○), 8 (□), 4 (△), and 2 μm (●).

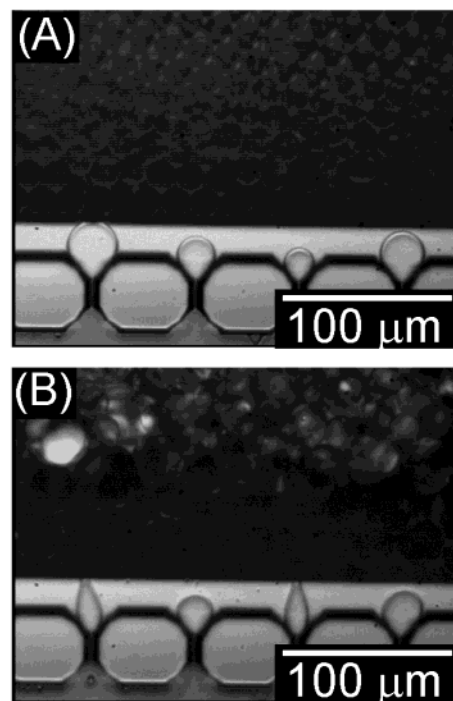


Figure 4. Microscope photographs of MC emulsification process below (A) and above (B) the critical velocity. The flow velocity of the dispersed phase is 0.5 (A) and 2.9 (B) mm/s.

Detachment time decreased slightly below the critical velocity, especially in smaller MCs (Figure 3). This phenomenon might be explained by the dynamic interfacial tension. At high

flow velocity in the dispersed phase, the formation rate of new interfaces increases, especially in smaller MCs. This leads to higher dynamic interfacial tension than at the equilibrium state. The higher dynamic interfacial tension may lead to shorter detachment times.

We studied the forces working in the MC emulsification in order to interpret the transition of the flow during MC emulsification. Flow characteristics in capillary systems are determined by the Reynolds number, which is expressed by the following equation:

$$[\text{Reynolds Number } (Re)] = \frac{\text{inertial force}}{\text{viscous force}} = \frac{\rho U d}{\eta} \quad (1)$$

where ρ is the liquid density, U is the characteristic velocity, d is the characteristic length, and η is the liquid viscosity. The transition point from laminar flow to turbulent flow can be estimated by the critical Re . Below the critical Re , viscous force is dominant, and the flow in a capillary is laminar flow. Above the critical Re , inertial force is dominant.

We applied the same logic to the transition of flow from spontaneous transformation to continuous outflow in an MC emulsification, assuming that the balance between interfacial tension and other forces determines the state of flow. The ratios between droplet-forming interfacial tension and other forces working in an MC emulsification can be estimated by the following dimensionless numbers:

[Bond number (Bo)] =

$$\frac{\text{gravitational force}}{\text{interfacial tension force}} = \frac{\rho g d^2}{\gamma} \quad (2)$$

[Weber number (We)] =

$$\frac{\text{inertial force}}{\text{interfacial tension force}} = \frac{\rho d U^2}{\gamma} \quad (3)$$

[Capillary number (Ca)] =

$$\frac{\text{viscous force}}{\text{interfacial tension force}} = \frac{\eta U}{\gamma} \quad (4)$$

where g is the gravitational constant, and γ is the interfacial tension. The experimental results showed that the critical point, at which the flow state changed drastically, was independent of d and was determined by U . Of the three dimensionless numbers shown above, Ca seems to be the appropriate determining factor for the state of flow because Ca does not include the term d and is proportional to U . The state of flow is determined by the value of Ca , which means the force balance between viscous force and interfacial tension force. If Ca is below the critical value, interfacial tension is dominant, the flow is based on spontaneous transformation, and monodispersed droplets are formed at intervals. If Ca exceeds the critical value, viscous force is dominant, the flow is similar to laminar flow, and the dispersed phase flows out continuously.

To confirm this idea, we investigated the droplet formation behavior using the dispersed and continuous phases with different viscosities and different interfacial tensions and MCs with different sizes. We performed MC emulsification while changing the flow velocity of the dispersed phase through the channel using different systems. Mixtures of triolein and castor oil, which have different viscosities, were used as the dispersed oil phase, and SDS aqueous solutions with different concentrations of PEG were used as the continuous phase for controlling the viscosities of the continuous phases. The viscosity ratio of the dispersed phase to the continuous phase was kept constant

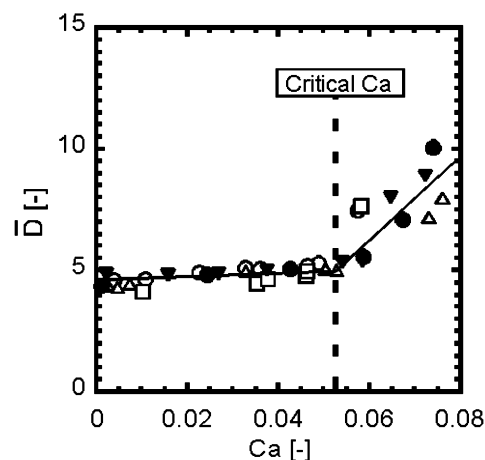


Figure 5. Dimensionless number plot of MC emulsification behavior with different viscosities, different MC sizes, and different interfacial tension. Experimental systems are 1 (○), 2 (□), 3 (△), 4 (●), and 5 (▼) which are shown in Table 2.

TABLE 2: Experimental Conditions Used in This Study

no.	MC depth [μm]	viscosity		viscosity ratio	interfacial tension [mN/m]
		dispersed phase [mPa s]	continuous phase [mPa s]		
1	8	588	10.5	56.0	5.9
2	16	588	10.5	56.0	5.9
3	8	288	5.10	56.4	5.7
4	8	181	3.29	55.0	5.3
5	8	151	2.77	54.4	2.9

in each experimental system. The different concentrations of SDS aqueous solutions were used for controlling the interfacial tension. Viscosities of the dispersed phases and continuous phases, interfacial tension, and MC size for each experimental system are shown in Table 2. MC emulsification was carried out at 25 °C.

SDS concentrations were 1% for experimental systems 1–4, and 3% for experimental system 5.

Figure 5 shows the relationship between Ca and the dimensionless droplet diameter. The viscosities of the dispersed phases were used to determine Ca . Dimensionless droplet diameter was defined using the following equation:

$$\bar{D} = \frac{D}{d} \quad (5)$$

where \bar{D} is the dimensionless droplet diameter, D is the droplet diameter, and d is the characteristic length of MC (MC depth). We selected MC depth as the characteristic length, because the MC depth is most significant parameter for the prepared droplet diameter.²⁰ \bar{D} is almost constant below the critical Ca and has the same values even though the MC size is different. In all experimental systems, \bar{D} suddenly increased above the critical Ca , which was independent of the viscosity, MC size, and interfacial tension. These results indicate that the law of similarity in MC emulsification applies when the MC geometry is analogous and the viscosity ratio (η_o/η_w) is constant. From these, it was shown that the state of flow (spontaneous transformation flow or continuous outflow) is determined by Ca .

Although the discussion above includes the essential physics underlying spontaneous transformation flow in MC emulsification, a complete description of the droplet formation is more complicated and depends on Ca , the viscosity ratio, the surface

properties of the MC, and the geometry of MC. However, the information obtained in this study is useful for determining the operating parameters in practical applications, such as the flow rate of the dispersed phase, the production rate of emulsions, and operating pressures.

4. Conclusion

We investigated the emulsification behavior using MCs with different sizes and analogous shapes and demonstrated that the state of flow changed drastically above the critical flow velocity. Below the critical velocity, the droplet-forming interfacial tension is dominant, and the state of flow is based on the spontaneous transformation caused by interfacial tension. Above the critical velocity, the interfacial tension is not dominant. The formed droplet diameters and detachment times drastically increased above the critical velocity.

The critical velocities were independent of MC size. Through dimension analysis, we were able to show that the critical point is determined by Ca . Below the critical Ca , interfacial tension is dominant, the flow is based on spontaneous transformation, and monodispersed droplets were formed. Above the critical Ca , the viscous force is dominant, and the flow is similar to laminar flow. The dispersed phase flowed out continuously, and polydispersed emulsions were formed. This was valid for the different viscosities of the dispersed and continuous phases, different MC sizes, and different interfacial tensions. These results indicated that the law of similarity in MC emulsification applies when the MC geometry is analogous and the viscosity ratio (η_o/η_w) is constant. The results obtained in this study include the essential physics underlying spontaneous transformation flow in MC emulsification and provide useful information about the operating parameters in practical applications.

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