Chemical Engineering Journal 101 (2004) 39–48

Chemical Engineering Journal

www.elsevier.com/locate/cej

Microchannel devices for the coalescence of dispersed droplets produced for use in rapid extraction processes

Yoshihito Okubo[a,*], Masaaki Toma[a], Hiroshi Ueda[a], Taisuke Maki[b], Kazuhiro Mae[b]

[a] *Process and Production Technology Center, Sumitomo Chemical Co. Ltd., 1-98 Kasugade-naka 3-chome, Konohana-ku, Osaka 554-8558, Japan*
[b] *Department of Chemical Engineering, Kyoto University, Kyoto, Japan*

Received 28 July 2003; accepted 28 October 2003

Abstract

A new microchannel device has been proposed for the assisted coalescence of dispersed droplets produced by a micromixer for use in rapid extraction. The microchannel was of rectangular cross-section and easily fabricated by placing a thin aluminum foil frame from which the shape of the microchannel was cut out between two flat plates made of glass and/or PTFE. The depth of the microchannel was adjusted by the thickness of the foil. The proposed device has several advantages such as a flexible and easily adaptable design, easy maintenance, and cheap setup without the requirement of microfabrication. The coalescence of the dispersed droplets occurred by passing through the microchannel, to attain liquid–liquid separation. Various liquid–liquid dispersion systems were examined and the coalescence mechanism of the dispersed droplets was also considered. Within the microchannel, the dispersion droplets are distorted, the liquid–liquid interface destabilizes, and a velocity differential between the continuous and dispersed phases brought about.

This proposed device will aid development of an efficient system for rapid liquid–liquid separation, which will allow extraction using a micromixing process to become a viable option in the near future.

Keywords: Microchannel; Dispersed droplets; Liquid–liquid extraction

1. Introduction

Liquid–liquid extraction is a very important unit operation in the chemical industry. The extraction consists of two steps. First, extracting a useful substance from an aqueous phase to an oil phase or an oil phase to an aqueous phase by mixing. And second, separation of the mixture into oil phase and aqueous phase is carried out to isolate the desired substance. Liquid–liquid extraction is used widely in fields such as chemistry, medicine, and food science.

At the micro-scale, the interfacial area per unit volume is very large, so it is generally suitable to carry out an efficient reaction and extraction operation via an interface. When using a microchannel as the extraction space, there are basically two known methods. The first method uses laminar flow in a microchannel, passing an extraction solvent and a reaction solution in the same direction and in the same channel, to extract the reaction product [1–3]. This method has the advantage that separation of the two phases can be performed easily by branching a flow near the exit. However, it is very difficult to maintain a liquid–liquid interface, for example, when using immiscible liquids such as water–organic solvents. It has been reported that in order to maintain a stable liquid–liquid interface, the microdevice used for the extraction operation has to be designed with special features [2,3]. However, in the case of this method, it cannot be denied that the device can only handle small volumes of liquid. The second method produces a two liquid mixture phase by distributing a reaction solution in the shape of droplets, and performing a quick liquid–liquid extraction, taking advantage of the increase in interfacial area. In the case of this method, it has been reported that the dispersed droplets may be formed using a micromixer and that quick extraction occurs [4]. This method may be used to deal with large volumes of liquid. If the dispersed droplets are merged completely within a short time period, a highly efficient extraction–separation system could be constructed using microprocessing in order to coalesce the stable dispersed droplets [5]. However, considering the future requirements for equipment able to handle large volumes of liquid, it is desirable to develop a simple and rational device and methodology which effectively employs the features of a micro-flow space.

---

[*] Corresponding author.
E-mail address: ookuboy@sc.sumitomo-chem.co.jp (Y. Okubo).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2003.10.025

Nomenclature

a	acceleration of a droplet (m/s^2)
a_{L}	acceleration of a large droplet (m/s^2)
a_{S}	acceleration of a small droplet (m/s^2)
$A_{2,\mathrm{L}}$	contact area between a large oil droplet and PTFE (m^2)
$A_{2,\mathrm{S}}$	contact area between a small oil droplet and PTFE (m^2)
$A_{3,\mathrm{L}}$	contact area between a large oil droplet and glass (m^2)
$A_{3,\mathrm{S}}$	contact area between a small oil droplet and glass (m^2)
F	force acting on the oil droplets (N)
F_1	force acting on the oil droplets due to continuous phase flow (N)
F_2	force which an oil droplet is subjected to by the PTFE wall (N)
$F_{2,\mathrm{L}}$	force which a large oil droplet is subjected to by the PTFE wall (N)
$F_{2,\mathrm{S}}$	force which a small oil droplet is subjected to by the PTFE wall (N)
F_3	force which an oil droplet is subjected to by the glass wall (N)
$F_{3,\mathrm{L}}$	force which a large oil droplet is subjected to by the glass wall (N)
$F_{3,\mathrm{S}}$	force which a small oil droplet is subjected to by the glass wall (N)
K_2	constant (–)
K_3	constant (–)
m	mass of an oil droplet (kg)
m_{L}	mass of a large oil droplet (kg)
m_{S}	mass of a small oil droplet (kg)
S_{L}	projection area of a large oil droplet (m^2)
S_{S}	projection area of a small oil droplet (m^2)
V	volume of an oil droplet (m^3)
V_{L}	volume of a large oil droplet (m^3)
V_{S}	volume of a small oil droplet (m^3)

Greek symbols

θ_1	angle in Fig. 9 (°)
θ_2	angle in Fig. 9 (°)
θ_3	angle in Fig. 9 (°)
θ_4	angle in Fig. 9 (°)
θ_{ad}	dynamic advance angle (°)
$\theta_{\mathrm{ad,g}}$	advance angle of water on glass (°)
$\theta_{\mathrm{ad,p}}$	advance angle of water on PTFE (°)
θ_{re}	dynamic retreat angle (°)
$\theta_{\mathrm{re,g}}$	retreat angle of water on glass (°)
$\theta_{\mathrm{re,p}}$	retreat angle of water on PTFE (°)

From this viewpoint, in this paper, a concept for a new microdevice and methodology for the coalescence of stable dispersed droplets is proposed. Attention is paid to the strong interaction between the surface of a wall and a fluid at the micro-scale. Various liquid–liquid dispersion systems are examined and the coalescence mechanism of the dispersed droplets is also considered.

2. Equipment and experimental method

2.1. Manufacture of the microchannel device

Fig. 1 shows schematically the structure of the microchannel device (MC device). The wall surfaces are glass and PTFE. The microchannel used was 10 mm in width and either 5 or 12 μm in depth. This device was easily fabricated by placing aluminum foil with thickness of 5 or 12 μm from which the shape (about 10 mm × 10 mm) of the microchannel was cut out, between glass and PTFE. An entrance and exit for the liquid–liquid dispersion phase was made on the glass wall, as shown in Fig. 2. The distance between the entrance and exit was set to 5 mm. The depth of the microchannel was adjusted by manipulating the thickness of the foil. As compared with other general microreactors whose design is more complicated, the assembly of this device has several advantages such as a flexible and easily adaptable design; it can also be maintained easily, and the setup is inexpensive without the requirement of microfabrication.

2.2. Measurement of the droplet-size-distribution

Water and dodecane were fed into the IMM micromixer with a channel width of 25 μm. The liquid–liquid dispersion produced was stabilized by introducing into a 0.5 wt.% sodium dodecyl sulfate aqueous solution (SDS; Wako Pure Chemicals Industries Ltd., Japan). The droplet-size-distribution of the dispersion phase was measured using a laser scattering particle size distribution analyzer (LA-920; Horiba Ltd., Japan), and the dispersion was observed by means of a digital microscope (VH-8000; Keyence Co., Japan). The total flow rate and the flow rate ratio of water and dodecane were changed, and droplet-size-distribution measurements were performed (Table 1). First, experiments in which the total flow rate was changed from 3 to 20 ml/min were conducted with the flow rate ratio of water and dodecane maintained at 9:1. Next, experiments in which the flow rate ratio was changed from 2:1 to 19:1 were conducted, with the total flow rate of water and dodecane maintained at 10 ml/min.

2.3. Dispersed droplets coalescence experiment

The dispersion was produced using two kinds of micromixer made by IMM and Yamatake Co. Ltd., YM-1 [7]. Liquid was supplied to the micromixer using two sets of micro-syringe pumps (IC3210; Kd Scientific Inc.). Dodecane and octanol were used for the dispersed phase. Droplet-size-distribution evaluations of the dispersion were performed using a laser scattering particle size distribution

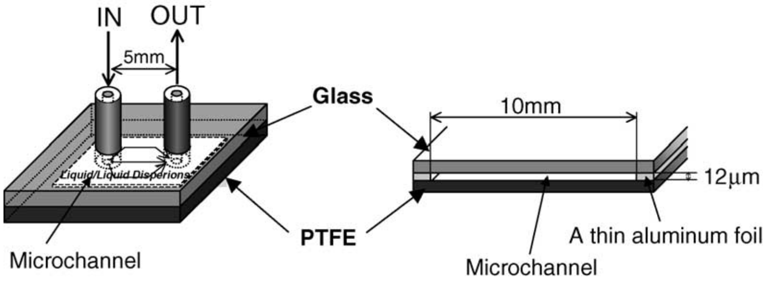

Fig. 1. Structure of the microchannel device.

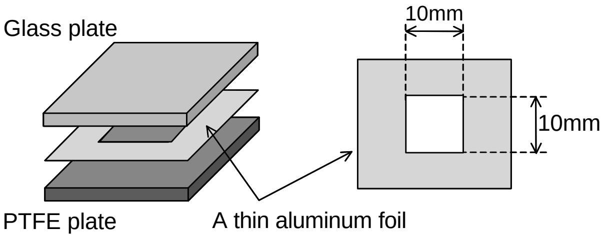

Fig. 2. Fabrication of the microchannel device.

analyzer and a digital microscope, after stabilizing it in 0.5 wt.% sodium dodecyl sulfate aqueous solution. Experiments were also conducted after changing the depth of the microchannel and its surface quality. Liquid was supplied to the MC device by the two methods discussed below. The experiments conducted are as shown in Table 2.

2.3.1. Method 1: direct supply from a micromixer

A silicone tube with length of 75 mm was used to directly connect the entrance of the MC device to the micromixer. An investigation was carried out to determine whether the dispersion made from the micromixer could be coalesced by the MC device. The amount of the dispersion supplied to the MC device per unit time was equal to the quantity supplied to the micromixer.

2.3.2. Method 2: using a liquid–liquid dispersion manufactured beforehand

The liquid–liquid dispersion was manufactured in advance and supplied to the MC device using a micro-syringe pump. The amount of liquid–liquid dispersion supplied to the MC device could be adjusted arbitrarily.

2.4. Contact angle measurement

Measurement of the dynamic advance angle, and the dynamic retreat angle of water in oil on the glass or PTFE, was performed using an automatic contact angle meter (CA-V; Kyowa Interface Science Co. Ltd., Japan). The contact angle value of a liquid which is discharged with force from a needle point and spreads on the glass or PTFE was collected for a series of time, and the dynamic advance angle was analyzed. In addition, the contact angle when liquid shortened by suction from the needle point was similarly analyzed and the dynamic retreat angle was obtained.

3. Results and discussion

3.1. Droplet-size-distribution measurement by a laser scattering particle size distribution analyzer

Fig. 3 shows the dispersed oil-in-water phase produced by an IMM micromixer with a channel width of 25 μm, with a feed rate of 2.7 ml/min of water and 0.3 ml/min of dodecane, as seen with a microscope. Fig. 4 shows the droplet-size-distribution measured with a laser scattering particle size distribution analyzer. Comparing with Figs. 3 and 4, it can be confirmed that the dispersed droplet-size-distribution measurement using with a laser scattering particle size distribution analyzer is almost exact.

Table 1
Experiments for the measurement of droplet-size-distribution

Continuous phase	Dispersed phase	Continuous phase flow rate (ml/min)	Dispersed phase flow rate (ml/min)	Flow rate ratio	Total flow rate (ml/min)
Water	Dodecane	18.0	2.0	0.111	20.0
Water	Dodecane	9.0	1.0	0.111	10.0
Water	Dodecane	5.4	0.6	0.111	6.0
Water	Dodecane	2.7	0.3	0.111	3.0
Water	Dodecane	9.5	0.5	0.0526	10.0
Water	Dodecane	9.0	1.0	0.111	10.0
Water	Dodecane	8.0	2.0	0.25	10.0
Water	Dodecane	6.67	3.33	0.50	10.0

Table 2
Experiments for coalescence

Experimental number	Continuous phase	Dispersed phase	Mixer	The supply method to the MC device	Continuous phase flow rate (ml/min)	Dispersed phase flow rate (ml/min)	The amount of supply to the MC device (ml/min)	Depth of the MC device (μm)	The undersurface quality of the material of the MC device
2-3-1	Water	Dodecane	IMM	Method 1	2.7	0.3	3.0	12	PTFE
2-3-2	Water	Dodecane	IMM	Method 1	2.7	0.3	3.0	100	PTFE
2-3-3	Water	Dodecane	IMM	Method 1	5.4	0.6	6.0	100	PTFE
2-3-4	Water	Dodecane	IMM	Method 1	2.7	0.3	3.0	12	Glass
2-3-5	Water	Dodecane	IMM	Method 1	5.4	0.6	6.0	12	Glass
2-3-6	Water	Octanol	YM-1	Method 2	20.0	5.0	0.3	12	PTFE
2-3-7	Water	Octanol	YM-1	Method 2	20.0	5.0	2.0	12	PTFE

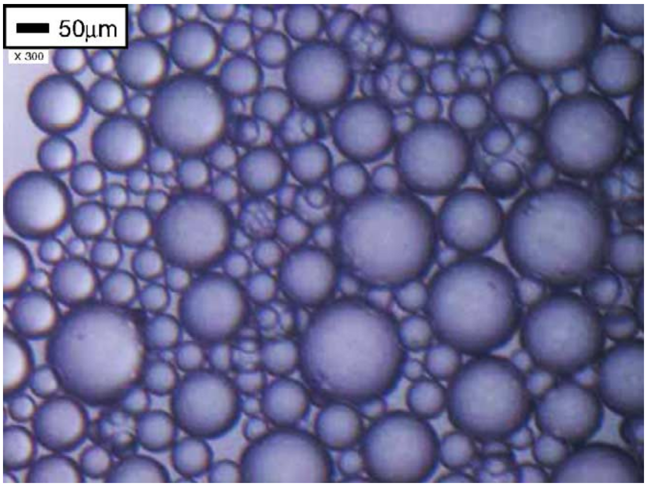

Fig. 3. Photograph of dispersed oil-in-water phase.

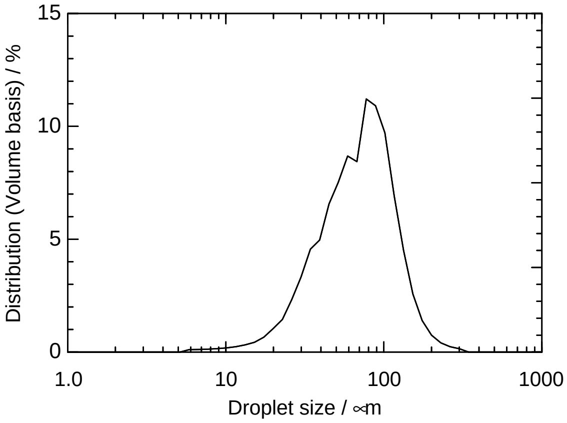

Fig. 4. Droplet-size-distribution of water–dodecane system.

Fig. 5 shows the droplet-size-distribution changes for tests in which the total flow rate was changed maintaining the flow rate ratio of water and dodecane at 9:1 supplied into the IMM micromixer. The dispersed droplet size is shown to become small as the total flow rate is increased, when the flow rate ratio was fixed. And it was confirmed that the dispersed droplet size becomes small as the dispersed phase ratio decreases, when the total flow rate is maintained at 10 ml/min. These results are in agreement with the reported result of Harverkamp et al. who evaluated droplet-size-distribution by microscope using water for the continuous phase and silicone oil for the dispersed phase [6].

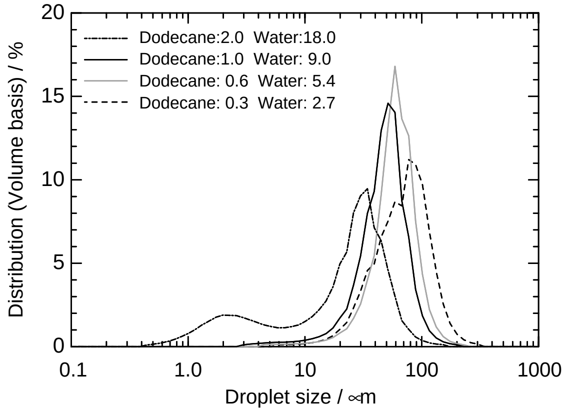

Fig. 5. Droplet-size-distribution change when the total flow rate was changed while maintaining the flow rate ratio.

3.2. *Coalescence of dispersed droplets*

3.2.1. *Water–dodecane system*

Coalescence was first examined for a water–dodecane system. Water was used for the continuous phase and dodecane was used for the dispersed phase. The liquid–liquid dispersion was produced using an IMM micromixer, and the liquid–liquid dispersion was introduced directly to the MC device as described in Method 1. When 2.7 ml/min of water and 0.3 ml/min of dodecane were fed into the IMM micromixer (experiment number 2-3-1), a dispersed oil-in-water phase layer was not visible in the exit liquid of the MC device. Separation into an oil phase and an aqueous phase had occurred almost completely. When the aqueous phase of the exit liquid was examined using a microscope, dispersed droplets were smaller than 10 μm as shown in Fig. 6 and only a very small quantity existed. From this, it was shown that dispersed droplets could be coalesced almost completely with a residence time as short as 0.01 s in a microchannel when the upper surface was glass, the lower surface was PTFE, and the channel depth was 12 μm.

Next, the influence of the microchannel depth on coalescence was considered. A polypropylene sheet with a thickness of 100 μm was placed on the MC device such that the microchannel depth became 100 μm (experiment numbers 2-3-2 and 2-3-3); comparative examinations of the degree of coalescence were carried out under same flow rate conditions. The results showed that when the depth of the microchannel was 100 μm, there was almost no difference

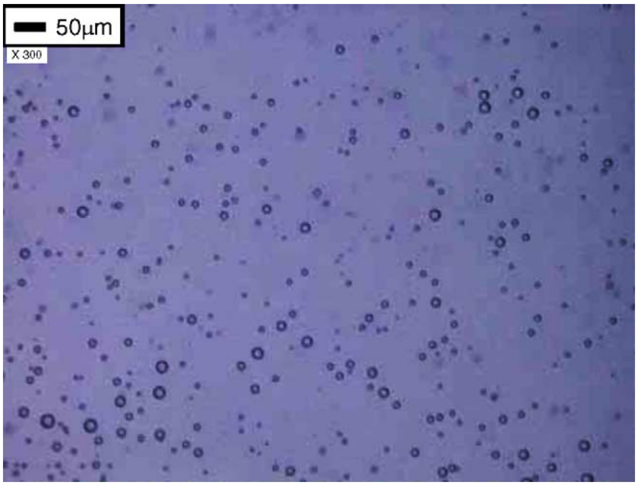

Fig. 6. Photograph of dispersed oil-in-water of the MC device.

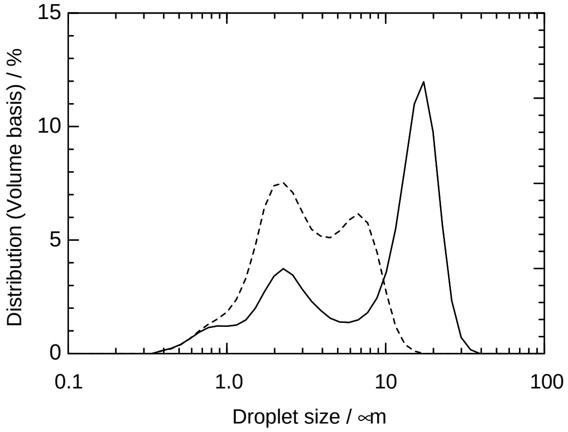

Fig. 7. Test for coalescence when the depth of microchannel is 100 μm.

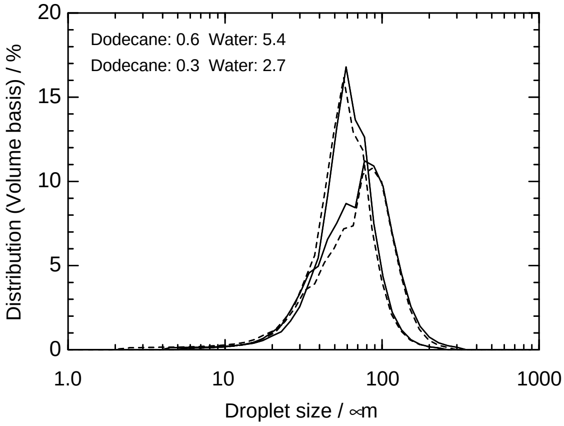

Fig. 8. Test for water–octanol system.

in the degree of liquid–liquid dispersion at the entrance and the exit of the MC device. The dispersed droplet-size-distribution before and after passing thorough the MC device is shown in Fig. 7. From Fig. 7, it can be seen that most droplets did not coalesce at all, simply passing through unchanged. From this, it became clear that the depth of microchannel is an important factor for coalescence.

For the next tests, the lower surface material of the MC device was changed to glass instead of PTFE, and the coalescence experiment was conducted using the MC device in which the surface of the microchannel walls constituted of only glass, to allow examination of the microchannel material. On comparing the influence of the microchannel material under the same flow rate conditions (experiment numbers 2-3-1 and 2-3-4), it was seen that coalescence of dispersed droplets did not occur when the MC device made only of glass was used, and an oil-in-water phase layer was observed in the exit liquid of the MC device. When the droplet-size-distribution of liquid before and after passing through the microchannel was measured, it turned out that there was almost no difference of droplet-size-distribution, and the dispersed droplets had not coalesced at all. This seems to suggest that the interaction between PTFE and a fluid greatly affects the coalescence process. However, due to the high pressure drop, a liquid–liquid dispersion can hardly pass through the MC device with both upper and lower surfaces constructed of PTFE.

3.2.2. Water–octanol system

The physical properties of an organic phase (viscosity, surface tension, polar group, etc.) greatly influence formation and coalescence of dispersed droplets. Therefore, the coalescence of octanol which forms hydrogen bonds with water, easily giving a stable oil-in-water phase, was considered. Water was used as the continuous phase and octanol was used for the dispersed phase. The liquid–liquid dispersion was produced beforehand using a YM-1 micromixer. As described in Method 2, the dispersion was supplied to the MC device with a microchannel depth of 12 μm at 0.3 ml/min via a micro-syringe. The droplet-size-distribution of the dispersion before and after passing through the MC device is shown in Fig. 8 for the case the flow rate was set at 0.3 ml/min, and the MC device with an upper surface of glass and an lower surface of PTFE was examined (experiment number 2-3-6). When dispersed droplets which have size distribution peaks around 2 and 18 μm passed thorough the microchannel, octanol droplets larger than 10 μm disappeared almost completely, and only octanol droplets smaller than 10 μm remained in the exit liquid of the MC device. On the other hand, in the experiment in which 2.0 ml/min outlet streams of the dispersion was supplied, there were almost no differences in droplet-size-distribution between inlet and outlet streams of the MC device (experiment number 2-3-7). Any change in the amount of oil-in-water phase was hardly noticeable. This result suggests that contact of droplets of the dispersion and the surface of a wall is a necessary condition for coalescence. It was also observed that the flow rate limit at which coalescence can occur is small when compared with the case of dodecane. This is thought to be due to the fact that a stable liquid–liquid dispersion is formed when the two compounds have a high affinity for each other. However, it became clear that the proposed device can coalesce dispersed droplets continuously with only a short contact time such as 0.12 s in the case of alcohols which associate with water.

3.3. Mechanism of the coalescence of dispersed oil droplets in the MC device

From the above results, it became clear that because the interaction of fluid and wall is important, the microchannel depth must be smaller than the diameter of the oil droplets for them to coalesce. The liquid–liquid separation of the exit liquid occurred completely, and it was apparent that coalescence of the dispersed droplets had taken place within the device. Putting these things together, it is expected that within the MC device a difference arises between the transfer velocity of water and that of the organic phase, and the

Table 3
Dynamic contact angles of water

	In dodecane		In octanol	
	Glass	PTFE	Glass	PTFE
θ_{ad} (°)	83	160	52	161
θ_{re} (°)	0	160	0	125

coalescence of oil droplets occurs through contact of the surface of a wall with the fluid. In order to examine this in detail, the dynamic advance angle, θ_{ad}, and dynamic retreat angle, θ_{re}, of water in dodecane and octanol were measured. As shown in Table 3, θ_{ad} and θ_{re} are less than 90° on glass and more than 90° on PTFE indicating that water in dodecane and octanol wets on glass and is repelled on PTFE. In particular, the fact that the value of θ_{re} on glass is 0° shows that water always spreads out on glass.

Based on this data, microchannel flow in the cases when the size of the dispersed droplets is larger than the depth of the microchannel and when it is smaller were considered separately.

3.3.1. *The case where the size of dispersed droplets is larger than the depth of the microchannel*

When the size of the dispersed droplets is larger than the depth of the microchannel, dispersed droplets must come into contact with the surface of a wall. In this case, the process by which coalescence takes place can be divided roughly into three subprocesses: (a) destabilization of the liquid–liquid interface due to the deformation of the dispersed droplets; (b) generation of a velocity differential between the continuous phase and the dispersed phase as a result of the interaction of the surface and the dispersed droplets; (c) the coalescence of the dispersed droplets. Each subprocess is examined in detail below.

3.3.1.1. Destabilization of the liquid–liquid interface due to the deformation of dispersion droplets. When the dispersed oil droplet size is larger than the depth of the microchannel, oil droplets deform within the microchannel, the surface area increases, and the interface is destabilized. From the dynamic contact angle data in Table 3, the deformation of the fluid within the microchannel may be depicted one-dimensionally as in Fig. 9(a). The angles θ_1, θ_2, θ_2, and θ_4 show the continuous phase water's retreat angle over glass, $\theta_{re,g}$, the retreat angle over PTFE, $\theta_{re,p}$, the advance angle over glass, $\theta_{ad,g}$, and the advance angle over PTFE, $\theta_{ad,p}$, respectively. Because $\theta_{re,g}$ for both dodecane and octanol is 0°, the continuous phase water is always spreading outwards on the glass wall.

3.3.1.2. Generation of a velocity differential between the continuous phase and the dispersed phase. In Fig. 9(a), because both $\theta_{re,p}$ and $\theta_{ad,p}$ are more than 90° on PTFE, the continuous phase water is repelled and a phenomenon called "slip" occurs. On the other hand, the dispersed phase wets and spreads out on the PTFE surface. This difference in the wettability between the continuous phase and the dispersed phase causes a velocity differential within the microchannel. Comparing to dodecane and octanol, the wettability of dodecane on PTFE is stronger than that of octanol on PTFE. This is in agreement with the fact that droplets of dodecane are coalesced even at high flow rates while octanol droplets are not. On the other hand, like Fig. 9(d), when both surfaces of the microchannel are glass as in Fig. 9(d), there is no velocity differential between the two phases because the oil droplets do not spread out on the wall surface, and so coalescence does not occur.

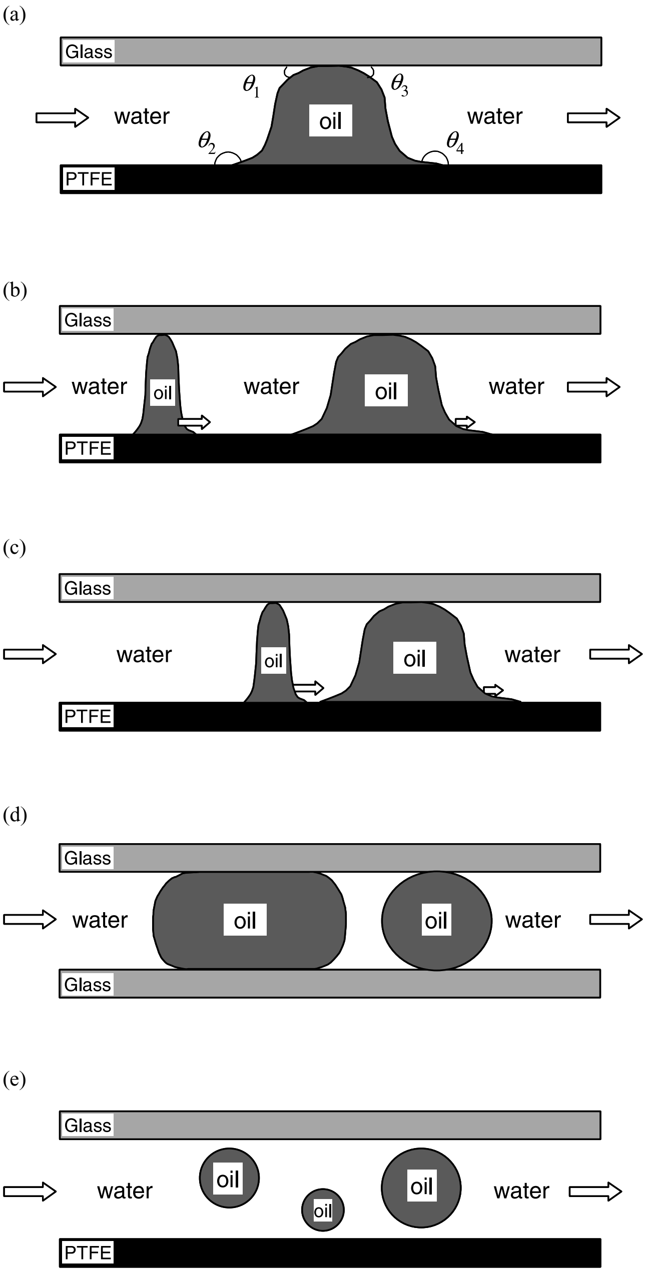

Fig. 9. Coalescence mechanism.

3.3.1.3. *Coalescence of the dispersion droplets.*

Because the velocity of the dispersed phase decreases relative to the continuous phase, coalescence of the dispersed droplets is promoted. Considering a simple, one-dimensional force balance on the droplets, the equation below is obtained.

The force F that acts on an oil droplet which has entered the microchannel is expressed as

$$F = F_1 + F_2 + F_3 \tag{1}$$

where F_1 is the force acting on the oil droplets due to the flow of the continuous phase, F_2 the force to which an oil droplet is subjected by the PTFE wall in the opposite direction to the flow of the continuous phase, and F_3 the force on an oil droplet attributable to the glass wall in the opposite direction to the flow of the continuous phase. Here, the volume of an arbitrary large oil droplet is set to V_L and that of a small oil droplet is set to V_S in the liquid–liquid dispersion.

The forces F_2 and F_3 which large oil droplets and small oil droplets are subjected to by the surface wall is proportional to the area of contact between an oil droplet and the surface of the wall. Here, $A_{2,\mathrm{L}}$ is the contact area between a large oil droplet and the PTFE wall, $A_{2,\mathrm{S}}$ is the contact area between a small oil droplet and the PTFE wall, $A_{3,\mathrm{L}}$ is the contact area between a large oil droplet and the glass wall, and $A_{3,\mathrm{S}}$ is the contact area between a small oil droplet and the glass wall. Vertically, the size of the droplets are limited by, and therefore equal to, the depth of the microchannel, then

$$\frac{A_{2,\mathrm{L}}}{A_{2,\mathrm{S}}} = \frac{V_\mathrm{L}}{V_\mathrm{S}}, \qquad \frac{A_{3,\mathrm{L}}}{A_{3,\mathrm{S}}} = \frac{V_\mathrm{L}}{V_\mathrm{S}} \tag{2}$$

The force on a large oil droplet attributable to the PTFE wall is $F_{2,\mathrm{L}}$, while that attributable to the glass wall is $F_{3,\mathrm{L}}$; likewise, the force on a small oil droplet attributable to the PTFE wall is $F_{2,\mathrm{S}}$ and that attributable to the glass wall is $F_{3,\mathrm{S}}$:

$$\frac{F_{2,\mathrm{L}}}{F_{2,\mathrm{S}}} = \frac{V_\mathrm{L}}{V_\mathrm{S}}, \qquad \frac{F_{3,\mathrm{L}}}{F_{3,\mathrm{S}}} = \frac{V_\mathrm{L}}{V_\mathrm{S}} \tag{3}$$

The force which an oil droplet is subjected to by continuous phase flow is proportional to the square of its relative velocity with the continuous phase, and the projection area of an oil droplet in the direction of flow.

The projection area of a large oil droplet is S_L and of a small oil droplet is S_S, then

$$\frac{S_\mathrm{L}}{S_\mathrm{S}} = \left(\frac{V_\mathrm{L}}{V_\mathrm{S}}\right)^{0.5} \tag{4}$$

If the force acting on a large droplet due to continuous phase flow is set to $F_{1,\mathrm{L}}$, and the force acting on a small droplet set to $F_{1,\mathrm{S}}$, then

$$\frac{F_{1,\mathrm{L}}}{F_{1,\mathrm{S}}} = \left(\frac{V_\mathrm{L}}{V_\mathrm{S}}\right)^{0.5} \tag{5}$$

Comparing to the force on large and small droplets, and considering Eqs. (1), (3), and (5), the following relationship is derived:

$$\frac{F_\mathrm{L}}{F_\mathrm{S}} < \frac{V_\mathrm{L}}{V_\mathrm{S}} \tag{6}$$

If the mass of a large droplet is set to m_L, and that of a small one to m_S, the equation for motion of an oil droplet may be expressed as

$$F = ma \tag{7}$$

And therefore

$$\frac{m_\mathrm{L}}{m_\mathrm{S}} = \frac{V_\mathrm{L}}{V_\mathrm{S}} \tag{8}$$

Here, the acceleration worked of a large droplet is set to a_L, and that of a small one is set to a_S. Immediately after entering the microchannel the oil droplets have a velocity equal to that of the continuous phase flow, independent of size. But once the oil droplets enter the microchannel, a difference in acceleration is generated. Small droplets then catch up with larger ones due to the difference in magnitude of the forces acting on them (from Fig. 9(b) and (c)). Upon catching up with a larger droplet, an oil droplet on the PTFE wall wets and spreads, coalescing in the process. Even if there is a difference in acceleration, however when the velocity of the continuous phase flow is large, the larger droplets are discharged from the MC device before smaller oil droplets have a chance to catch up with them, hence coalescence does not occur.

3.3.2. *The case where the size of a dispersed droplet is smaller than the depth of the microchannel*

As shown in Fig. 9(b), it is conceivable that oil droplets may collide due to inertial force and some of the droplets may coalesce even when the droplet size is smaller than the depth of the microchannel. However, oil droplets are discharged at the exit at almost the same velocity as the continuous phase, without being influenced by the wall of the microchannel.

When considering the above mechanism, it was presumed that conditions required for the coalescence of the dispersed droplets were as follows:

(I) The dispersed droplet diameter must be larger than the microchannel depth, because the droplets must deform in the microchannel to destabilize the liquid–liquid interface.

(II) The dispersed phase wets and spreads on the PTFE wall, and a velocity differential between the continuous phase and the dispersed phase occurs.

(III) The dispersion must be supplied to the MC device at a velocity such that the velocity differential between the continuous phase and the dispersed phase is enough that an oil droplet in contact with the wall to be caught up by a droplet surrounded by fluid which is behind it.

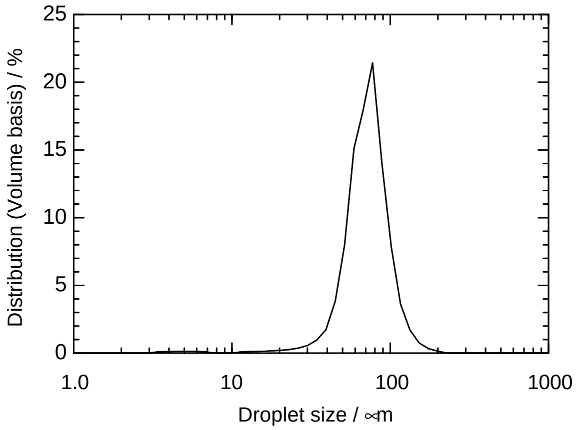

Fig. 10. Droplet-size-distribution of an emulsion with 1.0 wt.% sodium dodecyl sulfate aqueous solution as the continuous phase.

3.4. Application to a dispersion to which surfactant has been added

If a surfactant is added to the continuous phase, it is possible to produce a very stable dispersion using a micromixer. An emulsion of 1.0 wt.% sodium dodecyl sulfate aqueous solution (critical micelle concentration: 2.36 wt.%) as the continuous phase and dodecane as the dispersed phase was fed to the IMM micromixer at flows rate of 2.0 and 2.0 ml/min, respectively. The liquid–liquid dispersion produced was compared with an emulsion in which the continuous phase was without surfactant. In the case of only water was the continuous phase, there existed only a small amount of liquid–liquid dispersion immediately after production, and most of the dispersion phase disappeared within several hours. On the other hand, when a 1.0 wt.% sodium dodecyl sulfate aqueous solution was used as the continuous phase, the produced emulsion was cloudy due to a large dispersed proportion of dodecane shown in Fig. 11(a). Even when this liquid–liquid dispersion was left for 1 month, it was very stable and it did not visibly change.

The droplet-size-distribution of the emulsion produced using the 1.0 wt.% sodium dodecyl sulfate aqueous solution and dodecane at flow rates of 2.0 and 2.0 ml/min, respectively, are shown in Fig. 10. The measurements for the dynamic contact angle of 1.0 wt.% sodium dodecyl sulfate aqueous solution in dodecane are also shown in Table 4. It can be judged from the result of Fig. 10 and Table 4 that this liquid–liquid dispersion fulfills the above-mentioned conditions (I) and (II) required for the coalescence of the dispersion. When this liquid–liquid dispersion was supplied to the MC device with a channel depth of 5 μm, at a rate of 0.3 ml/min, good liquid–liquid separation was attained as shown in Fig. 11(b) and the dispersion layer was only barely visible in the exit liquid. In the case of the stable dispersion made from heptane and hexane as a dispersed phase and the 1.0 wt.% sodium dodecyl sulfate aqueous solution as the continuous phase, the same coalescence was observed. It became clear that this device is effective in coalescence of the dispersion droplets even when a surfactant added.

Table 4
Dynamic contact angles of 1.0 wt.% sodium dodecyl sulfate aqueous solution

	In dodecane	
	Glass	PTFE
θ_{ad} (°)	69	160
θ_{re} (°)	0	160

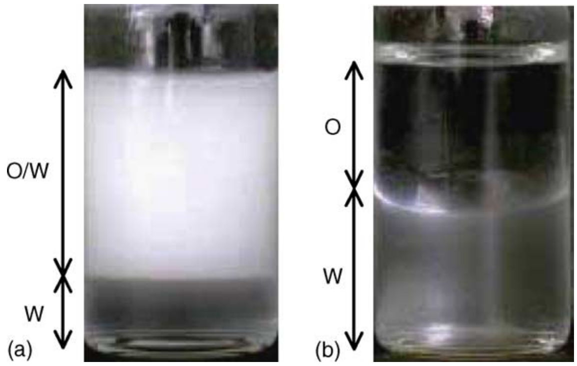

Fig. 11. Photograph of a dispersion made from dodecane and 1.0% SDS aqua.

4. Conclusion

In this paper, a new microchannel device was proposed which will aid the development of an efficient liquid–liquid extraction–separation system using a micromixer. This device uses the following features: (I) the dispersion droplets deform and the liquid–liquid interface destabilizes in a planar microchannel of rectangular cross-section; (II) the interaction between a PTFE wall and an organic phase has a strong influence on the bulk flow in a microchannel, and generates a velocity differential between the continuous and dispersed phases. It was shown to be possible to attain good liquid–liquid separation for that stable dispersion containing surfactant by supplying emulsion at a suitable velocity for that micro-space. There is a known method to coalesce dispersed droplets by forcefully filtering using PTFE or PE filters from before. However, this device essentially differs from filtering, even when the phenomenon is apparently the same. This device uses the difference in the dynamic contact angle between a liquid and the surface of a wall, and the dynamic contact angle can be precisely controlled by the surface conditions (configuration, coarseness, wetting property, etc.). That is, the aim of this device is the intentional control of the liquid–liquid interface in a micro-space.

This proposed device can be expected to contribute to fast improvement in the efficiency of industrial extraction operations. It could also be used as an attachment for macro-equipment by integrating a mechanism for handling large amount of dispersion, and is therefore not limited to use as a microchemistry system.

References

[1] T. Herweck, S. Hardt, V. Hessel, H. Löwe, C. Hofmann, F. Weise, T. Dietrich, A. Freitag, Visualization of flow patterns and chemical synthesis in transparent micromixers, in: W. Eherfeld (Ed.), Microreaction Technology: Industrial Prospects, Springer-Verlag, Berlin, Germany, 2000, pp. 171–180.

[2] M. Tokeshi, T. Minagawa, K. Ushiyama, A. Hibara, K. Sato, H. Hisamoto, T. Kitamori, Continuous flow chemical processing on a microchip by combining micro unit operation and a multiphase flow network, Anal. Chem. 74 (2002) 1565–1571.

[3] J. Shaw, R. Nudd, B. Naik, C. Turner, D. Rudge, M. Benson, A. Garman, Liquid/liquid extraction systems using micro-contactor arrays, in: Micro Total Analysis Systems 2000, Kluwer Academic Publishers, The Netherlands, 2000, pp. 371–374.

[4] K. Benz, K.-P. Jäckel, K.-J. Regenauer, J. Schiewe, K. Drese, W. Ehrfeld, V. Hessel, H. Löwe, Utilization of micromixers for extraction processes, Chem. Eng. Technol. 24 (1) (2001) 11–17.

[5] K.F. Jensen, Microsystems for chemical synthesis, energy conversion, and bioprocess applications, in: J. Yoshida (Ed.), Microreactors, Epoch-making Technology for Synthesis, CMC Publishing Co. Ltd., Japan, 2003, pp. 199–211.

[6] V. Harverkamp, W. Eherfeld, K. Gebauer, V. Hessel, H. Löwe, T. Richter, C. Wille, The potential of micromixers for contacting of disperse liquid phase, Fresenius' J. Anal. Chem. 364 (1999) 617–624.

[7] K. Mae, T. Maki, I. Hasegawa, U. Eto, Y. Mizutani, N. Honda, Development of a New Micromixer Based on Split/Recombination for Mass Production and its application to Soap Free Emulsifier, Chem. Eng. J., in press.