Bubble Splitting Under Gas–Liquid–Liquid Three-Phase Flow in a Double T-Junction Microchannel

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Gas–aqueous liquid–oil three-phase flow was generated in a microchannel with a double T-junction. Under the squeezing of the dispersed aqueous phase at the second T-junction (T2), the splitting of bubbles generated from the first T-junction (T1) was investigated. During the bubble splitting process, the upstream gas–oil two-phase flow and the aqueous phase flow at T2 fluctuate in opposite phases, resulting in either independent or synchronous relationship between the instantaneous downstream and upstream bubble velocities depending on the operating conditions. Compared with two-phase flow, the modified capillary number and the ratio of the upstream velocity to the aqueous phase velocity were introduced to predict the bubble breakup time. The critical bubble breakup length and size laws of daughter bubbles/slugs were thereby proposed. These results provide an important guideline for designing microchannel structures for a precise manipulation of gas–liquid–liquid three-phase flow which finds potential applications among others in chemical synthesis.

Keywords: microreactor, microfluidics, multiphase flow, bubble phenomena, bubble breakup

Introduction

Gas–liquid–liquid three-phase reactions are commonly encountered in various chemical syntheses, like hydrogenation,1–3 hydroformylation,4 and carbonylation.5 These reactions usually involve complex mass-transfer steps,6,7 including first the absorption of reactive gases (e.g., H2, syngas or CO) into the organic substrate phase and then the transfer of dissolved gases to the aqueous phase where a (homogeneous) catalyst is usually contained. This feature causes the overall reaction performance to be likely hindered by mass transport limitation. Therefore, an effective dispersion of reactants and large interfacial area are required to intensify gas–liquid–liquid mass transfer thereof. However, conventional reactors (e.g., stirred tank reactors) can hardly fulfill these requirements, leading to low reaction efficiency. Besides, these reactors usually exhibit poor controllability over the phase dispersion (e.g., by the presence of a broad distribution of bubble/droplet sizes, channeling and dead zones), and hence low reproducibility and poor predictability of product quality.

Microreactor is an attractive reactor type for carrying out these gas–liquid–liquid reaction processes by enabling effective mass transfer8–11 and precise process control.12–14 Yap et al.2,3 have shown that a series of hydrogenation reactions operated in a gas–liquid–liquid segmented flow (characterized by the alternate passage of bubbles and droplets in a continuous liquid carrier) yielded higher conversion and yield compared with its batch counterpart. Nevertheless, these reactions still remain mass transfer limited3 due to the nonoptimized dispersion of bubbles and droplets. Their microreactor design was simple (i.e., using capillary setups) and somehow arbitrary given a serious lack of common knowledge in the manipulation of three-phase flow in this field. In fact, their experiments already showed that shorter continuous phase segments improved mass transfer and reaction performance. Hence, it is inferred that by adjusting the dispersion of bubbles/droplets in a three-phase flow, mass-transfer rate may be improved by several folds, as reported in two-phase flow systems.15–17 This necessitates a comprehensive investigation into such topic for a successful application of three-phase reactions in microreactors. In addition, a precise control over gas–liquid–liquid flow
The existing numerous research on the breakup process of gas bubbles or liquid droplets in two-phase microchannel systems can shed light on the bubble breakup process in gas–liquid–liquid microfluidic systems. The presence of a second liquid phase would certainly increase the effect of phase interaction on the bubble breakup. The underlying rupture mechanism might thus differ significantly from that in two-phase systems. Therefore, efforts need to be taken for a better design and operation of three-phase microfluidic systems. This work concerns bubble breakup process under a gas–liquid–liquid flow in a microchannel with a double T-junction, aiming at improving the fundamental understanding thereof. Gas-oil segmented flow with slender bubbles was generated at the first T-junction, followed by bubble squeezing and splitting by the dispersed aqueous phase at the second T-junction. Types of the breakup regime, flow fluctuation, evolution of interfaces, and breakup time were presented and discussed. Subsequently, the critical bubble breakup length and size laws of daughter bubbles/slugs thereof were proposed.

Experimental Section

Microchannel device and experimental setup

The gas–water–oil three-phase flow experiments were performed in the microchannel device (under horizontal orientation) shown in Figure 1. The microchannel structure was fabricated on a transparent PMMA (polymethyl methacrylate) plate by precision milling technology (fabrication tolerance: 10 μm), covered by a second blind PMMA plate and sealed by bolted joints. All microchannels are 600 μm in width and 300
μm in depth and the serpentine main channel with half-circle connections is 44 cm long in total. The lengths of side channels 1, 2, 3 are 16, 40, 16 mm, respectively. The distance between the first and second T-junctions is 17 mm.

Oil and water were injected to inlet 1 and inlet 3 by syringe pumps (LSP02–1B, LongerPump, China), respectively. Gas was delivered from a cylinder to inlet 2 through a mass flow controller (SC200, Sevenstar, China) which was calibrated in advance. Thus, the gas–oil two-phase flow was formed at the first T-junction (abbreviated as T1) and the gas–water–oil three-phase flow at the second junction (abbreviated as T2). The experimental zone of interest is indicated by the blue dotted box in Figure 1. The three-phase flow in the main channel was recorded by a high-speed CMOS camera (Phantom M310, Vision Research, USA, working at 500–1000 frames/s) supplemented by an optical microscope (SZX 16, Olympus, USA).

**Experimental procedure**

In the experiments, nitrogen, aqueous glycerol solutions and n-octane with 2.5 wt % Span 80 were chosen as the working fluids. N-octane added with surfactants has lower interfacial tension than the aqueous counterpart, thus the oil phase acted as the continuous phase. Physical properties of these fluids are listed in Table 1. Viscosities were measured with a viscometer (DV-II + Pro, Brookfield, USA). Interfacial tensions between gas-phase/aqueous solutions and oil phase were measured by a tensiometer (DataPhysics OCA 15EC, Germany) using pendent drop method. Refractive indexes and densities were obtained from the literature. As can be seen, refractive indexes of the investigated aqueous solutions and oil phase are very close. Therefore, 0.02 wt % of methyl orange was added into the aqueous solutions to make it easier to distinguish the different phases. Adding such a small amount of methyl orange had little effect on the viscosity and interfacial tension according to our measurements. The experiments were performed at room temperature (20 ± 2°C) and ambient pressure, the flow rate ranges of oil, gas, and water phases being 0.10–0.30, 0.20–1.60, and 0.10–0.50 mL/min, respectively. Before recording the flow patterns, the system was running for at least 5 min to ensure the establishment of a stable flow.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fluid</th>
<th>Refractive Index</th>
<th>Viscosity μ (mPa·s)</th>
<th>Density ρ (kg/m³)</th>
<th>Interfacial Tension γ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>n-octane with 2.5 wt % Span 80</td>
<td>1.397</td>
<td>0.565</td>
<td>702</td>
<td>–</td>
</tr>
<tr>
<td>Gas</td>
<td>Nitrogen</td>
<td>1.000</td>
<td>0.018</td>
<td>1.271</td>
<td>21.94</td>
</tr>
<tr>
<td>Aqueous</td>
<td>Deionized water</td>
<td>1.333</td>
<td>1.002</td>
<td>1000</td>
<td>4.77</td>
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<tr>
<td></td>
<td>30 wt % glycerol</td>
<td>1.375</td>
<td>2.29</td>
<td>1078</td>
<td>4.94</td>
</tr>
<tr>
<td></td>
<td>50 wt % glycerol</td>
<td>1.404</td>
<td>5.28</td>
<td>1131</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>65 wt % glycerol</td>
<td>1.425</td>
<td>12.82</td>
<td>1171</td>
<td>4.69</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Breakup types and depression region evolution at T2**

To facilitate the interpretation of our results, several important notations are defined here. The segments of the continuous phase are referred as “plug” whereas the segments of dispersed aqueous droplets as “slug.” Bubbles generated at T1 are called parent bubbles and denoted by PB, as shown in Figure 2. If a parent bubble is cut-off by the aqueous phase at T2, the first generated daughter bubble is called DB1 and the second DB2. The aqueous slugs formed within the duration are defined as S1 and S2, accordingly. During these breakup processes, the depression region refers to the water area between the bubble and the channel wall (Figure 2). At the bottom of the depression region locates the stagnation point E, which is of the highest pressure and presets the droplet/bubble breakup point. A is the obstruction point, where the parent bubble touches the channel wall as the obstruction initially occurs. The operating conditions are expressed in the form of “oil flow rate-gas flow rate-aqueous flow rate (concentration of glycerol).” For example, “0.10–0.35–0.20 (0 wt %)” indicates that the oil and gas flow rates are 0.10 and 0.35 mL/min, respectively, and the aqueous phase is deionized water of which the flow rate is 0.20 mL/min.

At T2, three bubble breakup types were observed as shown in Figure 3: breakup with permanent obstruction (BPO), breakup with temporary obstruction (BTO) and nonbreakup (NB), which are similar to those observed in two-phase systems. Their characteristics are summarized as follows:

1. Type BPO (Figure 3a) mainly happens in surface-tension dominated systems with low viscous aqueous phases (e.g., deionized water and 30 wt % glycerol solution). In this breakup type, the bubble obstructs the main channel and pinches off S1 immediately once the front bubble cap creeps out of the T2 zone, that is, the obstruction point locates at the top-right corner of T2 (Figure 3a, upper image). The depression region is always symmetric with respect to the centerline of T2, and the stagnation point locates at the centerline (Figure 3a, middle image). When DB2 is about to leave T2, the aqueous phase is squeezed upward due to its lower surface tension compared with the bubble (Figure 3a, lower image). This may cause a large velocity fluctuation in the upstream flow.

![Figure 2. Important notations used in this article.](wileyonlinelibrary.com)
2. Type BTO (Figure 3b) mainly occurs in systems with high viscous aqueous solutions (e.g., 50 and 65 wt % glycerol solutions). The high viscosity of the aqueous phase makes slugs more difficult to be pinched off, resulting in the deformation of the front bubble cap. This also leads to the opening of a tunnel through which the aqueous phase flows downwards (Figure 3b, upper image). With the parent bubble creeping, the tunnel narrows gradually and thins out finally to yield the aqueous slug S1 (Figure 3b, middle image). We noticed that with more viscous aqueous phase, the obstruction point moves downward and it takes longer time for the tunnel to thin out (see Figure 3b, middle image, and Figure 3c, upper image). With higher ratio of the upstream flow rate to the aqueous flow rate (i.e., \(Q_{up}/Q_W\), where \(Q_{up} = Q_O + Q_G\)), the obstruction point also moves downward as shown in Figure 3c. After the tunnel disappears, an asymmetrical depression region with an off-center stagnation point is formed due to the high viscosity. Then the aqueous phase starts to squeeze and cut off the bubble neck (Figure 3b, lower image).

3. Type NB (Figure 3d) happens in systems with relatively short parent bubbles or large upstream flow rates. In this type, the extra aqueous slugs may be sheared off by the continuous phase (i.e., free ruptured slug).\(^{24,27}\) Thus, more than one slug can be generated between two bubbles downstream.

For bubble breakup, the interface evolution provides rich information to explore the underlying mechanism. Figure 4 presents an example of such evolution pattern based on the shape of the depression region in BPO. Shown in Figure 4a is the characterization of the depression region, which is illustrated by the left expanded length \(L_0\), the right expanded length \(L\), the width \(\omega\) and the location of stagnation point \(x_E\). Figure 4b depicts the evolution of these parameters from the parent bubble obstructing the channel to its breakup. As can be seen, the breakup process could be divided into three stages: the quick expansion stage, slow squeezing stage, and rapid collapse stage. The quick expansion stage starts at the moment when the parent bubble pinches off S1 and obstructs the channel totally \((t = 0)\). This obstruction induces quick augmentation of pressure in the aqueous phase, which further expands the depression region in both normal and tangential direction. During this stage, the stagnation point will be retracted back to the centerline \((x_E = 0)\) by surface tension.

![Figure 3: Bubble breakup processes in this microchannel device](image)

![Figure 4: Typical sketch of bubble breakup process](image)
Figure 5. (a) Independent case showing the instantaneous evolutions of the upstream and downstream bubble velocities and the aqueous phase flow rate. (b) The corresponding flow images for moments (1)–(7) in (a). The operating condition is 0.10–0.35–0.30 (0 wt %); The dotted vertical line in (a) shows the bubble breakup moment: $U/J$ equals $U_{up}A_{CW}/(Q_{O} + Q_{A})$ for the upstream flow and $U_{down}A_{CW}/(Q_{O} + Q_{A} + Q_{W})$ for the downstream flow.

[Color figure can be viewed at wileyonlinelibrary.com]

whereas its original location is a little downstream due to the effect of the inertial force during S1 formation. The retraction is also the reason of the fast increase of $L_{d}$, which characterizes the quick expansion stage.

In the slow squeezing stage, the bubble deformation is mainly driven by the applied water flow while the effect of the upstream pressure is very small. The expansion of the depression region mainly takes place in the $y$-direction when $L_{d} \approx L_{i} > \omega$. At this time, the shape of the depression region resembles to the bubble/droplet breakup in two-phase flow.33–36 However, when $\omega$ approaches $L_{i}$, the depression region keeps a semicircle shape ($L_{d} \approx L_{i} \approx \omega$) with three parameters increasing at the same pace. This shows that interfacial tensions start playing a dominant role over the upstream pressure and viscous force as $L_{d} \approx L_{i} \approx \omega$. It is in agreement with the phenomenon that the stagnation point E keeps staying at the $y$ axis.

When the depression region expands to a critical extent, it triggers the rapid collapse stage. At the critical time, the curvature at the stagnation point becomes the largest, which can easily lead to the spontaneous breakup of the bubble according to the surface-tension-driven mechanism proposed by Hoang et al.34 This mechanism suggests that the surface tension induces significant reverse flow to the stagnant point, which quickens the breakup. Besides, Wang et al.35 suggested that when the bubble neck is thin enough, the circulation flow around the bubble neck would also aggravate the Raleigh-Plateau instability and the bubble breakup.

The critical neck thickness in the case shown in Figure 4 is found as $\delta_{c}/w = 0.26$ (i.e., $= 1 - \omega_{c}/w$), which is in accordance with the literature.34–38 Afterwards, the bubble neck shrinks and the water contracts from the two sides dramatically (indicated by the rapid decrease of $L_{i}$ and $L_{v}$, and increase of $\omega$) till the bubble ruptures ($t = t_{b}$).

**Flow fluctuation**

The phenomenon that bubble neck obstructs the channel and ruptures periodically has been widely investigated in the bubble/droplet splitting29,34,35,37,38 or formation processes.42,43 These processes are always accompanied by the fluctuations of velocity and pressure. To gain a better understanding into the mechanism during bubble splitting in three-phase flow, we compared both the instantaneous bubble velocities in the upstream ($U_{up}$) and downstream ($U_{down}$) of T2. The bubble velocities were measured with Matlab (R2014b, The Mathworks, Inc., USA) by calculating the moving distance of bubble caps in a time step of 1–3 ms. We found that $U_{down}$ could be either independent of or in synchronization with $U_{up}$. The possible reason could be related to hydrodynamics in the aqueous phase, so we estimated the instantaneous aqueous phase flow rate ($Q_{EW}$) according to the captured 2-D images. The estimation included the extraction of the 2-D area of unbroken slugs in each frame, and then multiplying them with channel height to obtain the instantaneous volume of water. The difference in the consecutive volume values divided by the time step was approximated as $Q_{EW}$, which turned out to fluctuate largely during the bubble splitting process.

Figure 5 shows a typical case of $U_{down}$ varying independently with $U_{up}$. The time $t$ was scaled by bubble splitting period $T$. The measured $U_{up} (U_{down})$ and instantaneous $Q_{EW}$ were scaled by the corresponding superficial values $J_{up} (J_{down})$ and $Q_{W}$, respectively. Clearly, the normalized downstream bubble velocity $U_{down}/J_{down}$ keeps almost constant whereas the normalized upstream bubble velocity $U_{up}/J_{up}$ varies periodically under the specified operating condition. Similar to two-phase systems, the decline in $U_{up}/J_{up}$ occurs when the aqueous slug enters from the side channel to the main channel and leads to an increase in the flow resistance, whereas the rise in $U_{up}/J_{up}$ occurs when the augmented upstream pressure starts to release and leads to fast shrinkage of the slug neck.44–47 However, there are distinguishable characteristics for the three-phase system. As shown in Figure 5, the rapid decrease in $U_{up}/J_{up}$ from moment (3) to moment (5) originated from the increase in the flow resistance due to the slug tip squeezing the PB (moments [3]–[4]) and the slug blockage
after the bubble ruptures (moments [4]–[5]). Interestingly, the decrease in $U_{up}/I_{up}$ is larger after the bubble is pinched off. This suggests that the accumulation of flow resistance during the slug squeezing bubble is smaller than that during the slug blockage. It is reasonable as in the former case there is much larger space for the continuous phase flow around the bubble neck (especially, when the diameter of the bubble neck is smaller than the channel depth, i.e., $\delta < h$) when bubble is not pinched off. The next decline of $U_{up}/I_{up}$ from moments (6) to (7) is also due to the slug squeezing the DB2 and the slug blockage of the channel afterwards. As DB2 is not pinched off due to its relatively short length, neither dramatic shrinkage of bubble shape nor significant slope difference in $U_{up}/I_{up}$ exists during the evolution.

From Figure 5, it can also be seen that $Q_{EW}/Q_{W}$ varies just in the opposite phase of $U_{up}/I_{up}$, showing that the periodic pressure accumulation/release in the upstream flow and aqueous flow are also in the opposite phases. For example, when the aqueous phase is firstly blocked by the PB (moments [2] to [3]), the slug tip cannot squeeze the PB due to the stronger gas–oil interfacial tension. The instantaneous flow rate of the aqueous phase decreases rapidly while its pressure accumulates fast. As the augmented pressure becomes large enough to compete with interference tension, the bubble neck starts to shrink, leading to the pressure release in the aqueous phase (moments [3] to [5]). In the meanwhile, the flow resistance in the junction and the pressure of the upstream flow increase. In this way, the absolute flow fluctuations induced by the periodic generation of slugs are offset, which results in a much stable flow in the downstream (stable $U_{down}/I_{down}$).

For the synchronous case (Figure 6), which occurs under the breakup type with temporary obstruction (BTO), the normalized upstream bubble velocity $U_{up}/I_{up}$ also fluctuates periodically. But $Q_{EW}/Q_{W}$ is much more steady and steady compared with the independent case. In this case, the absolute fluctuation of $Q_{EW}$ cannot offset that of $U_{up}$, leading to a synchronous variation between $U_{down}/I_{down}$ and $U_{up}/I_{up}$. As can be seen, when $U_{up}/I_{up}$ increases from moment (1) to moment (3) due to the pressure release of the upstream flow, $Q_{EW}/Q_{W}$ only decreases significantly from moment (1) to moment (2). The generally stable aqueous flow from moment (2) to moment (3) results from the existence of an open tunnel which delays the pressure accumulation in the aqueous phase and further leads to the rebound of $Q_{EW}/Q_{W}$ postponed to the moment (4), close to the bubble rupture. This is totally different from the independent case in which the rebound of $Q_{EW}/Q_{W}$ occurs soon after T2 is blocked, as shown in Figure 5. As a result, there are several durations in which $Q_{EW}/Q_{W}$ varies very little and a significant fluctuation only occurs around the period during bubble breakup (moment [5]) and bubble cutting the slug (moment [1]). In addition, the fact that $Q_{EW}$ herein is relatively small compared with the upstream flow rate $Q_{up}$, the aqueous phase flow fails to compensate the fluctuation of $U_{up}$, and thus $U_{down}/I_{down}$ fluctuates in a synchronized pace with $U_{up}/I_{up}$.

Whether $U_{down}/I_{down}$ varies synchronically with $U_{up}/I_{up}$ depends on the viscosity of the aqueous phase $\mu_{W}$ and the upstream flow rate $Q_{up}$. As shown in Figure 7, the increase in $\mu_{W}$ by an increase in glycerol concentration can lead to a transition from the independent variation to the synchronous variation. Although, the magnitude of fluctuation in $U_{up}/I_{up}$ is very large at relatively low $\mu_{W}$ (e.g., with 0 wt % glycerol in the aqueous phase), it is nearly completely offset by the aqueous flow, leading to a stable $U_{down}/I_{down}$. At relatively high $\mu_{W}$, it usually induces the opening of a tunnel (i.e., breakup under BTO mode) which reduces the blockage of gas bubble. Therefore, the fluctuation in the aqueous flow rate tends to be smaller and cannot offset the fluctuation in $U_{up}$, leading to the synchronous variation. Meanwhile, the opening of the tunnel also reduces the squeezing force on the bubble. This results in the decreased magnitude of fluctuation in $U_{up}/I_{up}$ when $\mu_{W}$ increases (i.e., at increasing glycerol concentration).

Figure 8 shows the effect of the upstream flow rate ($Q_{up}=Q_{O}+Q_{G}$) on the flow fluctuation. It can be seen that...
increasing $Q_{up}$ has a similar effect to increasing $\mu_w$, that is, a transition from the independent variation to the synchronous variation tends to occur upon increasing $Q_{up}$. Though higher $Q_{up}$ results in both higher inertial force and viscous force exerted on the aqueous phase, the viscous force is not likely to dominate given the presence of the ultrathin oil film (thickness below the optic resolution: ca. $<20 \mu m$ as measured from the flow images) in the depression region and the less significant shear stress at the gas–oil interface due to the low gaseous viscosity. By contrast, it is more likely the inertial force that adjusts the squeezing direction of the aqueous phase and favors the tunnel opening, given somewhat large Reynolds number associated with the upstream flow (cf. Figure 9 which will be discussed in detail hereafter). The absolute velocity fluctuation in $U_{up}$ is observed to only increase slightly with the increase of $Q_{up}$. For example, the fluctuation ranges of $U_{up}$ are within 0.022, 0.023, 0.028 m/s for $Q_G = 0.35, 0.82, 1.54$ mL/min (or $J_{up} = 0.051, 0.094, 0.161$ m/s) in Figure 8, respectively. This results in an increased fluctuation in $U_{down}/J_{down}$ (Figure 8) due to the smoother $Q_{EW}/Q_W$ caused by the tunnel opening especially facilitated at higher $Q_{up}$ values (see Figure 3c). Although the decrease in the normalized fluctuation magnitude in $U_{up}$ (i.e., associated with $U_{up}/J_{up}$) on increasing $Q_{up}$ as shown in Figure 8 is partly caused by the increased denominator (i.e., $J_{up}$), this does signify the important effect of the inertial force in lowering the flow fluctuation in the upstream. In other words, without the effect of the inertial force in facilitating the tunnel opening at higher $Q_{up}$, the evolution of the depression region in all cases shown in Figure 8 should be under BPO mode. Then, at higher $Q_{up}$, the pressure accumulated in the upstream flow in this mode should be higher during the slug tip squeezing the PB (Figure 5b, moments [3–4]) and the slug blockage after the bubble ruptures (Figure 5b, moments [4–5]), which should result in a larger or at least the same magnitude of fluctuation in $U_{up}/J_{up}$ when it releases (Figure 5b, moments [5–6]).

From the analysis above, it is concluded that the velocity variation pattern is a result of the interaction among the phases...
at T2. Two main factors have been observed: the first one is the viscosity of the aqueous phase that influences the competition between the aqueous viscous force and interfacial tension; the other one is the upstream flow rate that influences the inertial force exerted on the aqueous phase. Therefore, \( Ca_w \) and \( Re_{up} \) are chosen to map the variation pattern of \( U_{up} \) and \( U_{down} \). \( Ca_w \) is defined in Eq. 1, which represents the importance of the aqueous viscous force over the interfacial tension.

\[
Ca_w = \frac{\mu_q Q_w}{\gamma_o \cdot \rho_{CH}} \tag{1}
\]

In the estimation of \( Ca_w \), the oil–gas interfacial tension \( \gamma_o,G \) is employed because it is the oil phase that directly touches the gas bubble and determines the bubble neck shape. The aqueous viscosity is adopted as the oil film is so thin that its velocity gradient is likely to be almost constant, implying that the shear force exerted on the gas–oil interface might be roughly equal to that on the oil-water interface (i.e., as if there is a direct shear action of the aqueous phase on the gas bubble).

\( Re_{up} \) is the Reynolds number of the upstream flow defined as

\[
Re_{up} = \frac{d_h(Q_0+Q_G) \rho_o}{\mu_q A_{CH}} \tag{2}
\]

The obtained map is shown in Figure 9, where five distinguished zones are identified as follows:

a. Zone I: the interfacial tension dominated zone. In this zone (\( Ca_w < 0.009-0.00015Re_{up} \)), the interfacial tension dominates over the aqueous viscous force and the upstream inertial force, and only the independent variation pattern is included.

b. Zone II: the transition zone where the interfacial tension is comparable to the viscous force or the upstream inertial force; both independent and synchronous variation patterns are observed in this zone. The transition line is depicted as \( Ca_w = 0.009-0.00015Re_{up} \).

c. Zone III: the aqueous viscous force dominated zone (\( Ca_w > 0.009 \) and \( Re_{up} < 60 \)), which only includes synchronous variation pattern.

d. Zone IV: the upstream inertial force dominated zone (\( Ca_w < 0.009 \) and \( Re_{up} > 60 \)). In this zone, the inertial force dominates over the viscous force and interfacial tension, and only the synchronous variation pattern is included.

e. Zone V: the synergistic zone of the aqueous viscous force and upstream inertial force (\( Ca_w > 0.009 \) and \( Re_{up} > 60 \)). As both forces facilitate the opening of tunnel, only the synchronous variation pattern is included.

It should be noted that the variation pattern is closely related to the breakup type, hence the map in Figure 9 can be used to distinguish types BPO and BTO: Type BPO mainly locates at zone I, while types BTO at zones III, IV, and V.

**Bubble breakup time and size prediction**

The critical bubble breakup length is an important parameter in the control of three-phase flow. For example, to achieve a quantitative dosing, the manipulation of a multistep synthesis process requires that the three-phase flow regime be kept in the nonbreakup zone. In two-phase flow, the critical droplet breakup length was proposed either by capillary instability or lubrication analysis. In three-phase flow, whether a parent bubble is split or not at T2 is governed by the rule that the time for the parent bubble passing T2 should be larger than its breakup time

\[
\frac{(L_{PB} - w_s)}{J_{up}} > t_b \tag{3}
\]

where \( w_s = w \) in the current microchannel. So the bubble breakup time needs to be derived first.

Leshansky et al. developed a 2-D model to illustrate the droplet breakup with permanent obstruction in liquid–liquid two-phase flow in a microfluidic T-junction, as shown in Figure 10. The model assumes that the shear force of the external flow (i.e., continuous flow in the case of Figure 10) is always balanced by the interfacial tension at point B, which means that the depression region keeps a steady-state evolution. Another assumption is that the depression region can be depicted as a circular arc with radius \( R(t) \) and a small angle \( \varphi \), thus, \( L_s = R \sin \varphi - R \theta \) and \( \omega = R(1-\cos \varphi) - \frac{1}{2} R \varphi \). For simplification, it is assumed that the continuous flow does not leak through the gap between the droplet and the channel wall. Thus, the increase rate of the area of the depression region \((\approx R^2 (\varphi - 1)/2 \sin 2\varphi) \approx 2R^3 \varphi^3/3)\) equals to the mean inlet flow rate

\[
\frac{d}{dt} \left( \frac{2}{3} R^3 \varphi^3 \right) \approx J_{CW} \tag{4}
\]

If the continuous phase perfectly wets the channel wall, the balance between the interfacial tension and viscous force around the depression region edge B can be described by the Tanner’s law, which suggests that \( \varphi^3 = \frac{2L_s}{\mu_c J_{CW}} \). Then, the expansion rate of the depression region \((dL_s/dt) \) reads

\[
\frac{d}{dt} (R \varphi) \approx \frac{2}{3 \mu_c \varphi^3} \tag{5}
\]

Where \( \mu_c = \mu_{CG} \). Solving Eqs. 4 and 5 yields the evolution of \( L_s \) and \( \varphi \) as

![Figure 10. Schematic of the depression region in a typical 'obstructed' breakup regime in two-phase flow in a microfluidic T-junction according to the model of Leshansky et al.](http://wileyonlinelibrary.com)
where $\alpha$ was approximated as 0.25 by fitting to 2-D numerical simulation results.\(^3\) Then the droplet breakup time is calculated as the time needed for the depression region width to be equal to the channel width ($w = w$)

$$t_b = 3.54 \frac{w}{J_c} \left( \frac{\alpha}{3Ca_c} \right)^{1/3}$$  

This correlation indicates that the droplet breakup time is negatively dependent on the capillary number of the carrier liquid ($Ca_c$).

The above model is firstly applied to describe the bubble breakup under BPO mode in gas–liquid–liquid three-phase system in this microchannel. It is expected to be approximately valid because all the aqueous phase squeezes the bubble without leakage due to the existence of the oil–water interface. In addition, the inertial of the upstream flow is very small compared with the interfacial tension in BPO, as shown previously in this article (e.g., see zone I in Figure 9). Therefore, the main deviation from this model is that the viscous force of the aqueous phase has to overcome the oil–gas interfacial tension as explained above (Eq. 1). This leads to a revision of the Tanner’s law\(^3\) as $\omega = \frac{w}{J_c} \left( \frac{\alpha}{3Ca_c} \right)^{-1/7} \left( \frac{J_c}{w} \right)^{3/7}$  

The usage of the aqueous viscosity is because that aqueous phase fills the depression region. Accordingly, the modified 2-D model of Leshansky et al.\(^3\) is obtained as

$$t_{b,L} = 3.54 \frac{w}{J_c} \left( \frac{0.25}{3Ca_w} \right)^{1/3} = 1.54 \frac{w}{J_w} Ca_w^{1/3}$$  

We compared the prediction of Eq. 9 with the experimental results and found that the prediction is about 10 times larger. There are two important reasons that result in this large discrepancy. First, the model developed from 2-D analysis deviates much from the real 3-D conditions. The prediction of the model of Leshansky et al.\(^3\) has also been shown to be 4–6 times higher than the simulated and measured bubble/droplet breakup time in two-phase flows.\(^3,4,14\) Hoang et al.\(^4\) found that the 2-D model can well predict the depression region in their 3-D simulation only before the bubble neck reaches the critical thickness ($h_b$). They proposed that the interfacial tension induced circulation near the neck could accelerate the breakup, which is, however, not considered in the 2-D model. The second reason is that the spread of the dispersed aqueous phase in x axis in three-phase flow is more difficult than that of the perfect wetting continuous phase in two-phase flow, which causes a much stronger squeezing on the gas bubble in y axis (e.g., see Figure 4a). This is reasonable since: (1) the squeezing phase in three-phase flow is the dispersed phase which is restricted by the oil–water interface, (2) the aqueous phase in three-phase flow cannot well wet the current microchannel wall made of PMMA preceding its expansion (due to the poor aqueous wettability, e.g., the deionized water–solid contact angle in the continuous oil phase is 135°) while the perfect wetting continuous phase does in two-phase flow. This also explains why the prediction of the 2-D model shows a larger divergence in three-phase flow than that in two-phase flow cases. Figure 11 shows the comparison between the 2-D model and our experimental results of $L_r$ and $\omega$. As can be seen, the experimental $L_r$ is much smaller, whereas $\omega$ is much larger than the model prediction at the later stage of the squeezing, suggesting that the spread of the aqueous phase in x axis is largely confined.

Accordingly, a semiempirical correlation similar to Eq. 9 is obtained for the breakup time under BPO mode through a regression of the experimental data

$$t_{b,P} = 0.165 \frac{w}{J_w} Ca_w^{1/3}$$  

where $t_{b,P}$ is the dimensionless breakup time scaled by $w/J_{up}$ in BPO mode. The range of the operating conditions is $0.0004 < Ca_w < 0.005$ and $0 < Re_p < 60$. And the same exponent associated with $Ca_w$ (i.e., $-1/3$ in Eq. 11) is used because it is thought that the model of Leshansky et al.\(^3\) is still approximately applicable to three-phase system, given many similarities in physical flow situation (or more precisely, in the governing equations of the interface evolution). Besides, a smaller coefficient (i.e., 0.165 here vs. 1.54 in Eq. 9) is obtained by adjusting the value of $\alpha$ (cf. Eq. 8) from 0.25 to 3.04 $\times$ 10$^{-3}$, which is acceptable because: (1) $\alpha$ is a fitting value resulting from sample data (i.e., either 2-D numerical simulation results\(^3\) or 3-D experimental results); (2) $\alpha$ fitted by 3-D experimental results tends to be much smaller than that by 2-D numerical simulation results\(^3\) due to the huge influence of the rapid collapse stage and much confined aqueous x-axial expansion on breakup time, as we have discussed previously (Figure 11).

As to the bubble breakup under BTO mode, the upstream flow plays an important role as previously mentioned (e.g., see Figure 9). Therefore, compared with Eq. 11, an additional modification over $t_{up}/J_w$ needs to be made here to depict the competition between the inertial force from the upstream flow and the squeezing from the aqueous phase. Then, a correlation for the breakup time in BTO mode is proposed as

\[ t_{b,P} = 0.165 \frac{w}{J_w} Ca_w^{1/3} \]  

\[ t_{b,P} = 0.165 \frac{w}{J_w} Ca_w^{1/3} \]
where $\text{t}_{b,T}$ is the dimensionless breakup time scaled by $w/J_{up}$ in BTO mode. The range of the operating conditions is $0.005 < C_d w < 0.022$ and $0 < Re_{up} < 100$. The positive exponent with $C_d w$ in this correlation is due to the existence of an open tunnel between the bubble and the channel wall. In BTO mode, the bubble breakup time consists of two parts: the tunnel time during which the aqueous phase flow through the tunnel, and subsequently the obstruction time during which the channel is obstructed by the bubble and the aqueous phase squeezes the bubble. The tunnel time is positively correlated to $C_d w$ (e.g., the tunnel width is shown to follow a law of $C_d^{0.029} w$ in two-phase systems $^{29,31}$) while the obstruction time is negatively correlated to $C_d w$ as indicated by Eq. 10. Therefore, it is reasonable that the tunnel time dominates over the obstruction time, resulting in a positive exponent with $C_d w$. It can be seen that both the predictions of Eqs. 11 and 12 agree well with the experimental results (Figure 12).

As the bubble breakup time is obtained, the critical bubble length and the size laws of daughter bubbles/slugs can be derived. According to Eq. 3, if the length of a PB is larger than its moving distance during the breakup time, the PB will rupture. A margin length equal to the side channel width ($w_s = w$ in our experimental conditions) was introduced in Eq. 3 as the squeezing starts when the bubble completely covers the side channel, as indicated by the simplified process shown in Figure 13 (i.e., at $t = 0$). However, we suggest this margin length to be $w + w_s$ as the blockage of the side channel is still needed when the bubble ruptures (i.e., $L_{DB2} \geq 1/2(w + w_s) = w$ in the current experiments). Thus, the critical bubble breakup length can be written as

$$L_c = w_0 = t_{b,T} + w + w_s$$  \hspace{1cm} (13)

According to the simplified model for the breakup process proposed in Figure 13, the lengths of $DB1$ and $DB2$ are then estimated as

$$L_{DB1} = w_0 + 1$$ \hspace{1cm} (14)

$$L_{DB2} = L_{PB} = 2$$ \hspace{1cm} (15)

It should be noted that the above analysis only considers the situation when a PB splits into two daughter bubbles. If a PB splits into more than two bubbles, $DB2$ can be treated as a new PB and the analysis is also applicable. In our experimental conditions, the splitting of $DB2$ only happens rarely in BTO mode with extremely long bubbles and very large aqueous flow rates. Figure 14 shows a comparison between the measured length of PB and the critical bubble length predicted by Eq. 13 in which $t_{b,T}$ was calculated by Eqs. 11 and 12 for BPO and BTO modes, respectively. As can be seen, a good prediction over whether the bubble breaks up or not is obtained in both modes (i.e., bubble is split at $L_{PB} \geq L_c$).
When a parent bubble breaks into two daughter bubbles under BPO mode, S2 is generated between them. The total generation time includes the bubble breakup time \( t_b \) and the time for DB2 to cut S2 off \( t_c \). The second time duration allows DB2 to move a distance of \( w_t \) as shown in Figure 13 \( t_c=(w+w_s)/U_{jup} \) \( w_s=w \) in the present experiments). Then, the length of S2 is derived as

\[
\frac{L_{S2}}{w} = \frac{J_W}{J_{up}} \left( t_b + t_c + \frac{w+w_s}{w} \right) = \left( t_b + 2 \right) \frac{J_W}{J_{up}}
\]

Besides, the frequency of the parent bubble equals to that of S1 and S2. If we neglect the slip velocity between bubbles and the aqueous slugs, the following equation holds approximately

\[
\frac{L_{PB}}{L_{S1}+L_{S2}} \approx \frac{J_G}{J_W}
\]

Therefore, the length of S1 could be estimated from

\[
\frac{L_{S1}}{w} = \frac{L_{PB}}{w} \frac{J_W}{J_{up}} = \frac{L_{S2}}{w} \frac{J_W}{J_{up}}
\]

As can be seen in Figure 15a, the proposed model (i.e., Eqs. 13–16, and 18) provides a good prediction over the lengths of daughter bubbles and slugs measured in our experiments under mode BPO. The small deviations are mainly caused by the flow fluctuations mentioned above. For example, during the generation process of DB1 (Figure 5, moments [1–4]), the average \( U_{jup} \) is higher than the corresponding superficial value (i.e., \( J_{up} \)) that is utilized in Eq. 14 for the calculation of \( \tau^* \), which results in the underestimation of \( L_{DB1} \) shown in Figure 15a as well as an overestimation of \( L_{DB2} \). Thus, it is expected that the smoother the flow fluctuation, the higher the prediction accuracy of this model. Interestingly, this proposed model also works well under BTO mode (Figures 14 and 15b), though the simplified breakup process shown in Figure 13 differs greatly from the real evolution process in BTO. This indicates that a good estimation of the bubble breakup time (e.g., Eq. 12) is essential in the size law prediction. As the detailed breakup mechanism under BTO mode is not very clear yet, more dedicated studies are still needed in this direction. It should be noted that this model is derived for the present microchannel with a double T-junction characterized by equal widths of side and main channels, thus its applicability in other configurations (e.g., with different side channel widths) still needs to be examined.

To further confirm the validity of our model, the measured \( L_{S2} \) values under mode BPO was compared in Figure 16 with the literature data (i.e., those obtained by Wang et al.24 during three-phase flow in a similar microchannel geometry; the original data in Figure 8 of their work were reprocessed to estimate the corresponding \( L_{S2} \) values as a function of \( J_W \)). As can be seen, the measured \( L_{S2} \) in our experiments follows a linear relationship with \( J_W \) for a given \( Q_{up} \) (or \( J_{up} \)) value, as indicated from Eq. 19 (which is derived from Eqs. 11 and 16)

\[
\frac{L_{S2}}{w} = \left( t_b + \frac{w+w_s}{w} \right) \frac{J_W}{J_{up}} = 0.165C_{aw}^{-1/3} + \left( 1 + \frac{w_s}{w} \right) \frac{J_W}{J_{up}}
\]

Furthermore, Eq. 19 also correctly reveals the decreased \( L_{S2} \) and linear slope with the increase of \( Q_{up} \) (or \( J_{up} \), as

![Figure 15. Comparison between the predicted daughter bubble/slug lengths and the experimental results: (a) type BPO; (b) type BTO. L_{DB1}, L_{DB2}, L_{S2}, L_{S1} are predicted by Eqs. 14–16, 18, respectively. [Color figure can be viewed at wileyonlinelibrary.com]](image)

![Figure 16. Comparison between our experimental results on L_{S2}/w (closed symbols) and those of the literature\(^2^4\) (+). Operating conditions in our experiments: the aqueous phase is deionized water, \( Q_w = 0.2–0.8 \) mL/min, \( Q_I = 0.28 \) mL/min, and \( Q_{up} \) is adjusted by the oil flow rate; Operating conditions in the literature\(^2^4\): \( Q_w = 0.182–0.512 \) mL/min, \( Q_I = 0.050–0.125 \) mL/min in the air-PEG aqueous solution-n-octane (with 2 wt % Span-80) system. [Color figure can be viewed at wileyonlinelibrary.com]](image)
The experimental results and is considered to be physically reasonable. The findings in this work can serve as an important guideline for the manipulation of flow regime/dispersion of gas–liquid–liquid flow in microreactors, which finds potential applications among others in chemical synthesis.

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Notation

- $A_{\text{CH}}$: cross-sectional area of microchannel [$A_{\text{CH}}=w h$, m$^2$]
- $d_h$: hydraulic diameter of main channel, m
- $h$: height of microchannel, m
- $J_c$: superficial velocity of the continuous phase [$J_c=Q_c/A_{\text{CH}}$, m/s]
- $J_{\text{down}}$: superficial velocity of the downstream bubble [$J_{\text{down}}=(Q_o+Q_0+Q_w)/A_{\text{CH}}$, m/s]
- $J_{\text{up}}$: superficial velocity of the upstream bubble [$J_{\text{up}}=(Q_o+Q_i)/A_{\text{CH}}$, m/s]
- $L_b$: critical bubble breakup length, m
- $L_{\text{DB1}}$: length of the first daughter bubble, m
- $L_{\text{DB2}}$: length of the second daughter bubble, m
- $L_{\text{d}}$: left expanded length of the depression region, m
- $L_p$: length of the parent bubble, m
- $L_{\text{r}}$: right expanded length of the depression region, m
- $L_{\text{s1}}$: length of the first aqueous slug, m
- $L_{\text{s2}}$: length of the second aqueous slug, m
- $Q_{\text{down}}$: preset downstream flow rate [$Q_{\text{down}}=Q_o+Q_w$, m$^3$/s]
- $Q_{\text{down}}$: instantaneous aqueous flow rate, m$^3$/s
- $Q_{\text{g}}$: preset gas flow rate, m$^3$/s
- $Q_{\text{o}}$: preset oil flow rate, m$^3$/s
- $Q_{\text{up}}$: preset upstream flow rate [$Q_{\text{up}}=Q_o+Q_i$, m$^3$/s]
- $Q_w$: preset aqueous flow rate, m$^3$/s
- $t_b$: bubble breakup time, s
- $t_{b,p}$: predicted bubble breakup time for BPO mode, s
- $t_s$: time that DB2 needs to cut $S_2$ off, s
- $t_{\text{DB}}$: instantaneous downstream bubble velocity, m/s
- $U_{\text{up}}$: instantaneous upstream bubble velocity, m/s
- $w$: width of microchannel, m
- $w_s$: width of side microchannel, m

Greek letters

- $\gamma_{\text{O-G}}$: interfacial tension between oil and gas, N/m
- $\gamma_{\text{O-W}}$: interfacial tension between oil and the aqueous phase, N/m
- $\delta$: neck thickness of bubble, m
- $\mu_o$: viscosity of the aqueous phase, Pa·s
- $\mu_i$: viscosity of the oil phase, Pa·s
- $\rho_o$: density of the oil phase, kg/m$^3$
- $\rho_s$: density of the depression region edge
- $\omega$: width of the depression region, m

Dimensionless groups

- $C_{a,c}$: capillary number of the continuous phase in two-phase flow [$C_{a,c}=\mu_c/J_c$]
- $C_{a,w}$: capillary number of the aqueous phase in three-phase flow [$C_{a,w}=\mu_w/J_c$]
- $Re_{\text{up}}$: Reynolds number of the upstream gas-oil flow [$Re_{\text{up}}=d_bQ_o/\mu_0\omega_s A_{\text{CH}}$]
- $t_{b,p}$: dimensionless bubble breakup time
- $t_{b,p}$: dimensionless bubble breakup time for BPO mode
- $t_{b,p}$: dimensionless bubble breakup time for BTO mode

Literature Cited


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