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Effect of mixing on mass transfer characterization in continuous slugs and dispersed droplets in biphasic slug flow microreactors

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HIGHLIGHTS

- Distribution patterns of transferred solute in slugs and droplets were visualized.
- Mass transfer in convection-dominated continuous slugs showed nearly-constant k_La .
- k_La in dispersed droplets decreased with τ under significant diffusion.
- Distinct correlations were used for mass transfer predictions in slugs and droplets.
- Dispersing the resistance phase into continuous slugs benefits system stability.

GRAPHICAL ABSTRACT

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ABSTRACT

The mass transfer of slug flow, a widely applied flow pattern in microreactors, is still difficult to predict mainly due to the competing nature between convection and diffusion. This work focused on the influence of the mixing mechanism on the mass transfer performance under gas-liquid and liquid-liquid slug flow, in both continuous slugs and dispersed droplets. Colorimetric study with the resazurin oxidation system was implemented, where the mass transfer resistance was constantly located in the aqueous phase. In the hydrophilic glass microreactor, the convection featured by intensive internal circulation and/or inter-slug leakage flow dominated diffusion, leading to nearly-constant k_La along the channel under given flow rates. However, in the hydrophobic PTFE capillary, the stagnant region constituted a significant share in the aqueous droplet, indicating the prominent role of diffusion against convection therein. As a result, k_La values decreased along the main channel length in fixed operating conditions. Accordingly, prediction models were respectively correlated depending on mixing mechanisms. Moreover, mass transfer contributions from the bubble and droplet formation stages were also investigated. This work is expected to shed light on judicious process design and reliable predictions in microreactor operations.

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1. Introduction

Over the past few decades, microreactors, which typically are chip-based microchannels or capillaries with lateral dimensions below ca. 1 mm, have received extensive attention. This microreactor platform has been widely used in academic researches and manufacturing industries especially towards the accessing of flash chemistry (i.e., with fast exothermic and/or kinetic features) [1–5], production of advanced intermediates for active pharmaceutical ingredients and fine chemicals [6–11]. The reason is due to the myriad of inherent benefits therein compared to conventional reactors, including large volumetric interfacial area, narrowed residence time distribution, elevated pressure endurance and substantially enhanced transport [12,13]. These advantages stem from the small dimensions (i.e., volumes) of microreactors and lead to more efficient (e.g., higher selectivity and yield [10,14–16]), safer [17] and point-of-use [6] chemical operations. Also, the production therein could be easily regulated by numbering-up [18,19], while preserving the optimized product qualities. Hence, microreactor technology as an innovative technology platform opens a new window to achieve flexible and robust chemical processes that are difficult to perform in traditional reactors.

For the most commonly encountered gas–liquid and liquid–liquid systems [4,9], the slug flow which is characterized by alternate continuous and dispersed segments has been most frequently adopted in microreactors, due to its precise control over segment sizes simply via flow rate ratios [20–22] and further against process performance [13,23]. For process intensification and microreactor design, reliable estimation over the mass transfer rate is inevitable, especially for mass transfer controlled systems [4,24]. As a result, empirical and/or semi-empirical correlations towards overall volumetric mass transfer coefficients $k_L a$ are often adopted in practical scenarios. However, contradictory results remain among various correlations reported in the literature. For example, most correlations of $k_L a$ are independent of the residence time [25–28], though clear evidence showed a decreasing trend along the channel (i.e., residence time increasing) [29,30]. This time-dependent $k_L a$ might be caused by the incorporation of mass transfer from the bubble/droplet formation stage, which might be higher than that in the main channel [31,32]. More fundamentally, the above contrasts are more likely to be caused by the difference in mixing intensity. Because the experimental $k_L a$ is typically calculated through the solute concentration obtained from sampling, which is an averaged value. But this averaged concentration may differ from the local concentration at the biphasic interface, leading to inaccuracy on the estimation of driving force and further to deviations between experimental and predicted $k_L a$ values.

To better understand the effect of mixing, here we look into two typical models respectively under convection-dominated and diffusion-dominated mixing. As shown in Fig. 1a, under an ideal case with perfect-mixing (typically in the gas–liquid system), van Baten et al. [25] proposed that $k_L a$ in slug flow could be assessed by the sum of separate

contributions from the slug bulk and the liquid film in a unit cell (i.e., $k_L a = k_{L, \text{cap}} a_{\text{cap}} + k_{L, \text{film}} a_{\text{film}}$). The mass transfer coefficients $k_{L, \text{cap}}$ and $k_{L, \text{film}}$ therein were evaluated by the penetration model, depending on the respective contact times. In specific, the contact time around the bubble cap was determined as a circulating liquid element sweeping over half of the bubble cap at the bubble velocity, while that in the liquid film was approximated by the time a liquid element passing through (i.e., $V_{\text{film}}/Q_{\text{film}}$, film volume divided by film flow rate) [25]. As these contact times are constant under given flow condition (i.e., bubble/droplet size, velocity), the obtained $k_L a$ remains constant along the channel. However, such perfect mixing is usually not fulfilled. In a physical extraction as shown in Fig. 1b, the transferred solute is more likely to concentrate nearby the interface in the solute-accepting phase (cf. droplet with red gradient color), but to be thinner at the interface in the solute-donating phase (cf. slug with blue gradient color), leading to a deviation between the actual concentration difference and the calculated one based on average values. With the expanding of such deviation along the channel, a significant decrease of measured $k_L a$ was observed [29,30,33–35]. Under the absolute dominance of diffusion (i.e., absence of convection), Susanti et al. [30] considered the entire interface surrounding the droplet as a curved stationary plane and estimated the corresponding contact time by the residence time. In consequence, the mass transfer coefficients in the continuous and dispersed phases were determined as $k_{L, C} = 2(D_C/\pi\tau)^{0.5}$ and $k_{L, D} = 2(D_D/\pi\tau)^{0.5}$ (D_C and D_D are corresponding diffusivities of the solute). Due to such intrinsic differences, the above models gave distinct predictions over mass transfer performance. Hence, it is critical to get insight into the mixing mechanism (i.e., the relative importance of convection and diffusion) for proper choice over models and reliable process predictions in biphasic slug flow operations.

For simplifying and decoupling the mass transfer processes, the main objective of this work is to investigate the mixing characterization respectively in the continuous slug and the dispersed droplet under biphasic slug flow, via separate operations in hydrophobic and hydrophilic microreactors. To obtain reliable experimental results (i.e., avoid outlet effect) and visual insights on internal circulation, the noninvasive colorimetric method, i.e., the oxidation–reduction of resazurin was applied [32,36–39]. In this visualization system, the resazurin solution was first reduced into the colorless dihydroresorufin outside microreactor, and then reacted with the oxygen-rich phase (air bubble or organic phase containing oxygen) into pink resorufin within the microreactor. This colorimetric reaction allows a negligible accumulation of oxygen molecules in the aqueous phase, without a significant chemical enhancement [37,40] (enhancement factor $E = 1.03$ – 1.06 in current work, detailed in Appendix). Hence, the measured $k_L a$ according to the color change in recorded images was closer to the physical values. Based on this, the internal circulation patterns and corresponding effects on mass transfer performance in the main channel were discussed, as well as mass transfer contributions during the droplet/bubble formation stage. Such insights are expected to deepen the understanding of the mass transfer process in slug flow, and to benefit researchers towards reliable mass transfer prediction and judicious process design in multi-phase operations for efficient synthesis of target chemicals using microreactors.

2. Materials and methods

2.1. Materials

Resazurin (sodium salt, CAS 62758–13–8, molecular mass: 251.17 g/mol) was purchased from Sigma Aldrich®, while glucose (CAS 14431–43–7), sodium hydroxide (CAS 1310–73–2) and *n*-octane (CAS 111–65–9) were ordered from Aladdin®. Deionized water was used to prepare the aqueous solution. Nitrogen and air came from Dalian Special Gases Co., Ltd.

Fig. 1. Illustrations of (a) perfect-mixing mechanism and (b) stationary diffusion scenario in biphasic slug flow. Solute concentration in each phase is indicated by the intensity of colors, the film thickness was exaggerated.

Fig. 2. Microchannel structure on the glass chip for the gas–liquid and liquid–liquid slug flows; view-sections are shown by blue and red boxes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Experimental set-up and apparatus

2.2.1. Gas–liquid and liquid–liquid slug flows in the hydrophilic microreactor

The glass-based microchannel structure is shown in Fig. 2. The microchannel is 600 μm wide and 300 μm deep, and the main section is composed of straight channel segments and the half-circle connections (i.e., $w = 600 \mu\text{m}$, $h = 300 \mu\text{m}$, radius $r_c = 1 \text{ mm}$, see ref. [38] for more structural details). In experiments, the aqueous solution (contained 0.3 g/L resazurin, 20 g/L glucose and 20 g/L sodium hydroxide) was flushed by nitrogen to remove dissolved oxygen, and subsequently injected into inlets 1 and 2 in equal flow rates via a syringe pump (LSP02-1B, LongerPump, China). For gas–liquid system, air from the pressurized gas bottle was calibrated by a mass flow meter (SC200, Sevenstar, China), and then delivered through an ultra-thin capillary

(inner diameter 20 μm , length 50 mm) to inlet 3. Alternatively, *n*-octane was also injected into inlet 3 via a glass syringe (Ruize Fluid, JYQ-50-1, China) for liquid–liquid study. The volumetric flow rates for the continuous phase Q_C and dispersed air/oil phase Q_D were respectively in the range of 0.3–1.6 and 0.2–1.0 mL/min. For simplicity, the operating conditions are expressed in the form of ‘Wx-Oy’, where x and y represent flow rates in mL/min. For example, ‘W0.2-O0.3’ refers to a liquid–liquid system with the aqueous and organic flow rates (i.e., Q_W and Q_O) being 0.2 and 0.3 mL/min, respectively. The same regulation was applied to all operating conditions in this work.

With the aid of an optical microscope (SZX 16, Olympus, USA), the biphasic slug flow within the microchannel was illuminated by a metal halide light source (MME-250, MORITEX SCHOTT) and recorded by a high-speed CMOS camera (Phantom M310, Vision Research, USA, working at 100–500 frames/s). As shown in Fig. 2, The view section indicated by the blue dashed box was recorded with a low magnification ($\times 0.8$, with a resolution of 0.0176 mm/pixel) to monitor the phase dispersion, while a higher magnification ($\times 2.0$, resolution 0.0071 mm/pixel) was adopted for mass transfer characterization (red box). Images were taken after the system reached stabilization ($\geq 5 \text{ min}$).

2.2.2. Liquid–liquid slug flow in the hydrophobic microreactor

The liquid–liquid slug flow was also operated in a PTFE capillary with 0.5 mm inner diameter (i.e., $d = 0.5 \text{ mm}$) and 1.6 mm outer diameter, where the aqueous phase was dispersed as droplets. As presented in Fig. 3, the capillary was implanted into a 10 cm-long immersion pool on the PMMA chip, to avoid the black margins in recorded images. In operation, the immersion pool was filled with *n*-octane, images (resolution as 0.0082 mm/pixel) were taken by the same optical set in section 2.2.1. As shown by the inserted images in Fig. 3b, the image taken from the immersion pool (right image) was much clearer than that from ambient circumstances (left image). The channel lengths L_c between shooting points and the T-mixer were respectively 65, 95, 115, 135 and 155 mm. Q_O and Q_W were respectively in the range of 0.2–1.0 and 0.6–1.6 mL/min.

The properties of these involved fluids were summarized in Table 1, where the viscosities and surface tensions were respectively measured by a viscometer (DV-II + Pro, Brookfield, USA) and a tensiometer (DataPhysics OCA, 15EC, Germany). Besides, oxygen concentrations in *n*-octane and air phases were respectively $C_{O,0} = 2.10 \times 10^{-3} \text{ mol/L}$ and $C_{G,0} = 8.18 \times 10^{-3} \text{ mol/L}$, while its maximum consumption under full conversion of resazurin in the aqueous phase was $C_{\text{max}} = 5.97 \times 10^{-4} \text{ mol/L}$. That is to say, oxygen was in excess in current operations. The diffusivity of oxygen in organic phase D_O was reckoned by Stokes-Einstein equation, i.e., $D_O = D_W \mu_W / \mu_O = 7.3 \times 10^{-6} \text{ cm}^2/\text{s}$.

Fig. 3. (a). Visualization setup and (b) the corresponding sketch for liquid–liquid slug flow in the PTFE capillary. The immersion pool was indicated by the blue dashed box and scaled by the short red lines in 1 cm interval. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1Physical properties of working fluids (20 ± 2 °C, 0.1 MPa).

Phase	Fluid	Viscosity μ [mPa·s]	Density ρ [kg/m ³]	Surface tension γ [mN/m]
Organic	n-octane	0.565	702	49.67*
Gas	air	0.0179	1.184	–
Aqueous	0.3 g/L resazurin with 20 g/L glucose/sodium hydroxide	1.29	1002	73

* Interfacial tension with the aqueous phase

⁹ m²/s [30], which was higher than that in the aqueous phase ($D_W = 3.2 \times 10^{-9}$ m²/s [37]). The partition coefficient of oxygen in the organic and aqueous phase was approximated by the ratio of their saturated concentrations in air, resulting in $m = 10.08$. Due to such high diffusivity and concentration in the organic phase, the mass transfer resistance in the liquid–liquid system was most likely to lie in the aqueous phase. All experiments were conducted at room temperature (20 ± 2 °C) and ambient pressure (0.1 MPa).

2.3. Color calibration and image processing

To quantify the mass transfer performance, the molar concentration of transferred oxygen C was first calibrated with the grey differences (ΔG) between corresponding images and the blank, resulting in a ΔG - C calibration curve. In the rectangular glass microreactor, though with the existence of the channel corner and the thin film around bubbles/droplets, the vast majority of the aqueous phase resided uniformly in the continuous slug, making the calibration procedures much easier (elaborated in ref. [38]). However, in the capillary microreactor, the aqueous droplet was composed of a typical cylindrical body and two semi-spherical caps. From the top-view, each row of pixels in the radial direction was related to a specific depth and hence altered the grey values in captured images (cf. Fig. 4). According to such variations, the capillary area in each image was divided into 5 slices and calibrated respectively, resulting in either quadratic or linear correlations (Fig. A2). Note that a pixel-to-pixel calibration is technically practical, but this strategy would complicate the calibration and calculation processes and amplify the errors caused by noises, especially for pixels near the wall. The current 5-slice method resulted in a reasonable error of 10% (see Appendix), which is comparable to that of the glass microreactor (below 10% [38]). The ΔG - C calibration curves of both reactors were used to abstract the distribution of normalized equivalent oxygen concentration C_{norm} ($=C/C_{\text{max}}$) and then visualized in a colormap fashion [38].

Fig. 4. Color calibration for capillary microreactor in 5 slices (colored in the top-view) according to the depth, which was denoted in the side-view.

Fig. 5. Size laws of (a) dispersed bubbles/droplets and (b) continuous slugs against flow rate ratio for the gas–liquid and liquid–liquid slug flows in the hydrophilic microreactor.

3. Results and discussion

3.1. Gas–liquid and liquid–liquid slug flows in the hydrophilic microreactor

3.1.1. Dispersion sizes

Phase dispersion determines the interfacial area and is crucial for the mass transfer in microreactors [33,41]. Fig. 5 shows that the lengths of dispersed segments were well scaled by $L_D/w = 1.67 + 1.96Q_D/Q_C$ for both the gas–liquid and liquid–liquid systems. Likewise, and the slug length was linearly correlated by $L_S/w = 1.69 + 0.98Q_C/Q_D$. Such linear scaling law has been illustrated by Garstecki et al. [20] in their pioneering work ($Ca < 10^{-2}$ and $Re < 1$), where the bubble/droplet generation processes under squeezing regime were divided into two ideal stages: (1) channel blocking stage, where bubble/droplet tips were characterized with channel dimension w ; (2) squeezing stage,

where the continuous phase squeezed the bubble/droplet neck (initial width w) at a speed of $J_C (=Q_C/w)$ till pinch-off (squeezing time w/J_C), while the bubble/droplet grew at a speed of $J_D (=Q_D/w)$. Consequently, the total bubble/droplet length was determined as $L_D/w \sim 1 + \beta Q_D/Q_C$. But these ideal squeezing processes do not usually happen in practice. Considering the leakage flow, Van Steijn et al. [21] modified the above model to $L_D/w = \alpha + \beta_1 Q_D/Q_C$ in a square channel. Likewise, Völkel [22] proposed that the slug length should be scaled as $L_s/w = \beta_1 + \alpha Q_C/Q_D$. Overall, the linear correlations in Fig. 5 indicate that slug flows here ($Ca = 0.8\text{--}6.3 \times 10^{-3}$) were generally under the squeezing regime [20], though the mismatched fitting parameters (α and β_1) in these two correlations imply that the original assumption of squeezing regime was not fulfilled. This is reasonable because the inertial force played a more prominent role in the bubble/droplet formation process here (i.e., $Re = 20\text{--}100$). Moreover, it also increased the leakage flow through channel gutter and the squeezing time, resulting in longer bubbles/droplets [42–44].

3.1.2. Mass transfer in bubble/droplet formation stage

In this work, the mass transfer in the bubble/droplet formation stage was determined by the averaged equivalent oxygen concentration C_{ave} in the slug right after the newly generated bubble/droplet, as framed by the dotted red box in Fig. 6. Considering the absence of free oxygen molecules in the aqueous phase and the mass conservation of transferred oxygen therein, $k_L a$ was derived as [36,37]

$$k_L a = \frac{C_{ave} J_W}{L_c C^*} \quad (1)$$

where J_W is the superficial velocity of the aqueous phase ($=Q_W/w$) and C^* ($=2.55 \times 10^{-4}$ mol/L [37]) is the equilibrated oxygen concentration in the aqueous phase under air. L_c in this work always refers to the distance between the center of the 2nd T-junction and the center of the interested zone (here the slug center denoted by blue '+', as shown in Fig. 6d). a is the volumetric interfacial area of the dispersed phase, which was estimated by the polygonal cross-section of bubble/droplets in the glass microreactor [38,45] and the round cross-section in capillaries [30]. Thus, the mass transfer coefficient k_L was obtained by dividing $k_L a$ by a . For the liquid–liquid system, C^* was replaced by the mean concentration difference ΔC_m between the inlet (denoted by subscript 0) and location L_c (subscript 1):

$$\Delta C_m = \frac{(C_{O,0}/m - C_{W,0}) - (C_{O,1}/m - C_{W,1})}{\ln\left(\frac{C_{O,0}/m - C_{W,0}}{C_{O,1}/m - C_{W,1}}\right)} = \frac{C_{O,0} - C_{O,1}}{m \ln(C_{O,0}/C_{O,1})} \quad (2)$$

where $C_{O,1}$ was obtained by mass balance within the focused area

Fig. 6. Mass transfer in the bubble formation stage. The focused slug was shown by the dotted red box, while its center was denoted by blue '+', operating condition: G0.2-W0.3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Volumetric mass transfer coefficients $k_L a$ during bubble/droplet formation stages for (a) gas–liquid and (b) liquid–liquid slug flows in the hydrophilic microreactor.

(i.e., $C_{O,0}Q_O = C_{O,1}Q_O + C_{ave}Q_W$).

As shown in Fig. 7, $k_L a$ in bubble and droplet formation stages for gas–liquid and liquid–liquid systems both decreased with the residence time $\tau (= (Q_C + Q_D)/A_c)$, and could be respectively fitted by $k_L a = 0.012\tau^{-0.905}$ ($R^2 = 0.79$) and $k_L a = 0.065\tau^{-0.995}$ ($R^2 = 0.91$). This is because that the cases with short residence time here happened under higher Q_{tot} ($=Q_C + Q_D$; cf. Fig. A3), leading to intensified surface disturbance and larger leakage flow through channel corner [43,44]. Compared to the liquid–liquid flow, $k_L a$ values from gas–liquid flow were more scattered, due to the higher Q_C/Q_D ratios employed and more evident flow fluctuations [46] caused by the compressibility of the gas. Furthermore, the $k_L a$ values in the liquid–liquid system ($1\text{--}5\text{ s}^{-1}$) were higher than those in gas–liquid systems ($0.1\text{--}0.8\text{ s}^{-1}$). This is because the generation regime under liquid–liquid flow slightly shifted from squeezing to transitional/dripping due to lower interfacial tension, which opened a larger gap between the droplet and the channel wall. On the other hand, the transport of oxygen from octane to the aqueous phase (transfer free energy = 11.92 kJ/mol) was thermodynamically easier than that from gas (solvation free energy = 26.48 kJ/mol) [47,48]. Considering that $k_L a$ values in the main channel for both systems were in the range of $0.5\text{--}2.5\text{ s}^{-1}$ (Fig. 12), it seems that the mass transfer in the formation stage was inferior (reduced by 75% for gas–liquid flow) or comparable (increased by 1 time for liquid–liquid flow) to that in the main channel. The large deviation

of the contribution from the formation stage was also reported in the literature. Ganapathy et al. [49] concluded that k_{La} in the bubble formation stage was reduced by $> 50\%$ compared to that in the main channel in T-junction capillaries, via a 2D simulation. In contrast, Yang et al. [32] demonstrated that k_{La} values in the bubble formation stage were larger than those in the downstream by 28–64% under the same resazurin system. This is mainly because that (1) the cross-junction in their work created more contact area than the T-junction in the present work (Fig. 6); (2) with 1.0 g/L resazurin solution (corresponding $C_{\max} = 2.0 \times 10^{-3}$ mol/L) and small $Q_G/Q_W (= 0.2-0.25$, $C_{G,0} = 8.18 \times 10^{-3}$ mol/L), the oxygen content was almost in deficit, making the shearing-induced circulation within the bubble tip more important [31]. Meanwhile, Bai et al. [50] found that k_{La} values at the droplet formation stage within T- and cross-junctions were 3–4 times higher than that in the main channel, though droplet sizes therein were much smaller than channel width. Conclusively, ratios of k_{La} from formation stage and the main channel were in the magnitude of $O(10^{-1}) \sim O(10^0)$, but the exact values could vary significantly in case-specific, depending on the mixing structure, dispersion configuration and distribution of mass transfer resistance. Thus, more in-depth investigations are required for a better understanding.

3.1.3. Mass transfer in the main channel

To investigate the mass transfer in the main channel, the oxygen concentrations in the 2nd, 3rd and 4th straight channels were abstracted from images with high magnification ($\times 2.0$, cf., Fig. 2). The locations were fixed at $L_c = 27.06$, 44.24 and 71.80 mm respectively, corresponding to residence times $\tau = 0.1-1.5$ s. As shown in Fig. 8, given a specific operating condition, the experimental k_{La} for both gas-liquid and liquid-liquid slug flows hardly varied with the increase of residence time, which agrees with the intrinsic definition of k_{La} under convection-dominated transport scenario. Nevertheless, such an intrinsic feature is easy to be covered by insufficient convection inside the aqueous slug and/or scarcity of the resazurin reactant in the aqueous phase. For example, with the same resazurin system, Yang et al. [33] reported that the measured k_{La} was reduced along the channel length as $\tau = 1-5$ s. This is because: (1) the large channel dimension ($w = h = 2$ mm) abated the intensity of internal circulation; (2) the reaction rate of oxygen with low resazurin concentration (0.1 g/L, corresponding $C_{\max} = 0.199 \times 10^{-3}$ mol/L vs. $C^* = 0.255 \times 10^{-3}$ mol/L) might be smaller than its physical transport rate, especially when resazurin conversion approached 100%, leading to the presence of oxygen molecules at the interface or even in the slug bulk. In a recent work of the same group [34], the time-related k_{La} was also presented in an FEP circular tube ($d = 1$ mm, 0.1 g/L resazurin solution) under non-wetting slug flow (i.e., the liquid film was absent), which largely attenuated the internal mixing [51]. In comparison, the wetting slug flow within rectangular microchannel in the current work induced evident leakage flow and intensive internal circulation (will be explained in the following text), together with the low conversion of resazurin (mostly $< 60\%$) allowed us to obtain the intrinsic k_{La} in the current residence time range. In other words, the mass transfer here was dominated by convection within the aqueous slugs [35,52].

To further verify the assertion of convection-dominated mixing in the aqueous phase, the distribution of normalized equivalent oxygen concentration (C_{norm}) was investigated. As shown in Figs. 9 and 10, two distinct distribution patterns were observed. Fig. 9 displays a typical mal-distribution pattern occurring under relatively small flow rates, where C_{norm} in the lower half slug was higher than its upper counterpart (Fig. 9a). This pattern has also been observed and explained by the convection at the channel bends in one of our previous studies [28]. As depicted in Fig. 9b, the concentrated filaments were aggregated at the right-lower section of the bend (marked with the red circle), and then confined within the separate circulation loops in the following straight channel (Fig. 9c, $L_c = 44.44$ cm). Though with such confinement, the streamlines were obviously stretched, separated and recombined

Fig. 8. Development of volumetric mass transfer coefficients k_{La} along residence time (i.e., channel length) for (a) gas-liquid and (b) liquid-liquid slug flows in the main channel of the hydrophilic microreactor.

($L_c = 39.54-42.18$ cm in Fig. 9c). Thus, the mass transfer could still be convection-controlled. From the practical aspect, this mal-distribution could be detrimental for mixing-sensitive processes, e.g., highly exothermic or highly selective reactions [5,53], hence intensification methods such as passive structures [54] and higher flow rates should be considered. Fig. 10 demonstrates the even-distribution pattern of C_{norm} in slugs along width-wise under relatively high flow rates, where the concentrated filaments were however gathered at the leading cap of the bubble (red boxes in Fig. 10b and Fig. 10c at $L_c = 39.95$ mm). In the following straight channel, the concentrated bolus surprisingly bypassed the bubble through the channel gap and flowed into its downstream slug (Fig. 10c, $L_c = 39.95-44.93$ mm and video A1). The periodic in- and out-flow of such liquid bolus indicated a considerable amount of forward leakage flow through channel corners [43,44], which substantially enhanced the overall mass transfer rate. Till now, one could see that the distribution patterns were highly influenced by the fluidic hydrodynamics within the bend.

As explained above, the mass transfer distribution patterns were highly related to hydrodynamics within the bend, which is governed by the forces exerted on the filaments therein: interfacial tension, inertial force, viscous and centrifugal forces. To illustrate the relative importance of these forces, the dimensionless Ce number was adopted to compare the centrifugal force and the interfacial tension [41], as

$$Ce = \frac{\rho_w J_{tot}^2 d_h^2}{\gamma_w r_c} \quad (3)$$

where J_{tot} is the total fluid velocity ($= (Q_w + Q_g) / wh$). Likewise, the inertial and viscous forces were compared by Re number. Accordingly, the mass transfer distribution patterns were mapped as shown in Fig. 11. For the gas-liquid system, the mal-distribution case occurred under low Ce and Re values ($Ce < 0.07$ and $Re < 60$), where the interfacial tension and viscous force dominated the inertial and centrifugal forces. Yet, the even-distribution pattern happened under high Ce or Re values ($Ce > 0.10$ and $Re > 70$), where inertial and/or centrifugal forces governed interfacial tension and the viscous force. Under $0.07 < Ce < 0.10$ and $60 < Re < 70$, transitional cases were observed. Similarly, such distribution patterns also presented in liquid-liquid systems. But the aforementioned critical boundaries are slightly changed as $Ce = 0.08, 0.12$ and $Re = 50, 60$, respectively. The distribution map indicates that increasing the bend curvature or flow rate would shift the distribution pattern from mal-distribution to even-distribution, if needed.

For application purposes, the measured $k_L a$ was compared to empirical and semi-empirical correlations developed under the slug flow context [28,55]. Among them, many showed either no relevance [30] or poor correlation coefficients [25,56] (Fig. A5), while the semi-

Fig. 11. Map of mass transfer distribution patterns over Ce and Re numbers.

theoretical correlation proposed by Yao et al. [28,55] gave very good predictions within 20% deviations for both gas-liquid and liquid-liquid systems (cf. Fig. 12), as

Fig. 10. Even-distribution pattern of normalized equivalent oxygen concentration C_{norm} in slugs (a) in the central area of straight channels (magnification $\times 2.0$), (b) within and (c) right after the 2nd circular bend (magnification $\times 0.8$). White '+' denotes the slug center. Operating condition: G1.0-W1.6, flow direction: left to right.

Fig. 12. Comparison of experimental volumetric mass transfer coefficients $k_{L,a}$ and the predicted values for gas-liquid (O) and liquid-liquid (X) slug flows in the hydrophilic microreactor, with locations denoted in the legend.

$$k_{L,a} = \frac{2\sqrt{2}}{\pi} \sqrt{\frac{D_W J_{tot}}{d_h} \frac{4}{L_{uc}}} + C a^{0.349} \frac{2}{\sqrt{\pi}} \sqrt{\frac{D_W J_{tot}}{L_D} \frac{4L_D}{L_{uc} d_h} \left(\frac{L_D}{L_s}\right)^{-0.534}} \quad (4)$$

where L_{uc} is the length of the unit cell ($= L_D + L_s$). This correlation inherited the basic idea of separate contributions from the slug bulk and the liquid film proposed by van Baten et al. [25], but additionally considered the mixing between the two parts, instead of the simple perfect-mixing assumption. Therefore, the modified correlation could better reflect the mass transfer in the practical condition, e.g., the mass transfer contribution from the aqueous film (second term in Eq. (4)) constituted about 5–35% of global $k_{L,a}$, indicating the (partial) saturation of the aqueous film [57,58]. More importantly, Yao et al. [28,55] have demonstrated its validity for various flow conditions, channel structures and fluid properties in both gas-liquid and liquid-liquid slug flow systems. They have also stated that this correlation was developed when the mass transfer resistance mainly lies in the continuous phase, and its utilization under similar conditions was recommended. In conclusion, the good performance of Eq. (4) in the present systems, together with the strong convection explained above, confirmed that the mass transfer resistance located in the continuous aqueous phase for both gas-liquid and liquid-liquid slug flows.

3.2. Liquid-liquid slug flow in the hydrophobic capillary

To obtain more profound insights on the effect of mixing on biphasic mass transfer, the liquid-liquid slug flow was also investigated in the hydrophobic PTFE capillary (inner diameter 0.5 mm), where the mass transfer resistance mainly located at the aqueous droplet. As shown in Fig. 13, the experimental $k_{L,a}$ under fixed flow rates decreased monotonically with the increase of residence time, differentiating from those observed in the hydrophilic microreactor (Fig. 8). The reason is speculated to be a more prominent effect of diffusion within the droplet than that in the continuous slug. As analyzed above, the continuous aqueous slug in the rectangular hydrophilic microreactor benefited from the strong circulation and leakage flow, resulting in the dominance of convection over diffusion and constant $k_{L,a}$ along the channel. However, within aqueous droplets, the intensity of internal circulation is supposed to be weaker [59], because the circulation therein is induced by the interfacial shearing between two phases with relative motion, instead of the friction by the stationary wall [60–64]. Besides, the leakage flow is not possible in droplets. Overall, the effect of diffusion probably was comparable to that of the convection. Note that the more important role of diffusion (or less evident convection) does not

Fig. 13. Development of volumetric mass transfer coefficient $k_{L,a}$ with residence time under liquid-liquid slug flow in the hydrophobic capillary.

necessarily lead to smaller $k_{L,a}$ values. Compared to glass microreactor (Fig. 8b), $k_{L,a}$ values shown in Fig. 13 did not see significant decreases, some were even higher. This is because the oxygen in the *n*-octane droplet was in excess ($C_{O,0} \approx 3.5C_{max}$). In the glass microreactor, the dihydroresorufin within the thin aqueous film was likely to be significantly consumed, causing the deactivation of the film area. However, in PTFE capillary, the volume of aqueous droplet body was much larger than that of the surrounding organic film, resulting in more oxygen transported to the aqueous phase. That is to say, the actual availability of the biphasic interface and the transport mechanism determined the global $k_{L,a}$ together. If the film was activated, the overall mass transfer rates in the hydrophilic microreactor are expected to be higher.

To justify the speculation of the non-negligible diffusion effect, the local distribution of equivalent oxygen within droplets was examined. As shown in Fig. 14, a different distribution pattern rather than those in continuous slugs was observed. The transferred oxygen was accumulated mainly at the posterior half of the droplet and minorly at the anterior section, while the oxygen-deficient stagnation zone was permanently located at the anterior half of the droplet. The enrichment of transferred oxygen near droplet caps was caused by the faster droplet velocity, which leads to stronger surface disturbance and more intensive circulation nearby droplet caps [65]. Whereas, the transport of the transferred solutes was impeded around the stagnation zone, leading to the phenomenon that the oxygen accumulation therein resembled that in a stationary plane, as displayed in Fig. 14a. Hence, the diffusion within aqueous droplets played a significant role against convection. In this work, we also implemented the gas-liquid-liquid flow to show the effect of droplet size on the concentration distribution. As shown in Fig. 14b, with the addition of nitrogen gas, a droplet was cut off into two daughter-droplets of different lengths [66], the stagnation zone constituted a larger portion in the smaller droplet. Namely, the development of convection was somehow confined in smaller droplets, which should be considered for the mass transfer characterization.

In line with the significant effect of diffusion in the current hydrophobic capillary, it is reasonable to establish the mass transfer correlation based on the diffusion-dominant assumption, i.e., the model of Susanti et al. [30] presented in the introduction section (for more comparisons with other models [29,67,68], see Fig. A5). By a simple estimation ($k_{L,W} = 2(D_W/\pi\tau)^{0.5}$ and $k_{L,O} = 2(D_O/\pi\tau)^{0.5}$), we noticed that the mass transfer resistance in aqueous droplet was 15.2 times of its organic counterpart ($1/k_{L,W} = 15.2(1/mk_{L,O})$). Thus, the resistance from the organic phase could be ignored. Besides, an additional term

Fig. 14. Distribution of equivalent oxygen concentration in (a) aqueous droplets under liquid-liquid slug flow and (b) daughter-droplets of different lengths that were cut off by nitrogen bubbles in the hydrophobic capillary. The colormaps were enlarged from the focused areas outlined by red dashed boxes. Locations and operating conditions were denoted in texts, flow direction: left to right. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Q_W/Q_O was introduced to characterize the effect of droplet length (Fig. A4) on the development of mixing, resulting in

$$k_L = 5.01 k_{L,W} \left(\frac{Q_W}{Q_O} \right)^{0.1762} \quad (5)$$

where the fitting coefficient 5.01 represented the intensification of internal circulation based on diffusion. Fig. 15 presents that Eq. (5) provided excellent predictions towards k_L within a deviation of 15%. In contrast, Susanti et al. [30] reported a smaller fitting coefficient of 2.6 (i.e., $1/k_L = 2.6(1/k_{L,W} + 1/mk_{L,O})$, without Q_W/Q_O term) in the extraction of acetanilide from aqueous droplets to octanol slugs, where the mass transfer resistance was mainly in aqueous droplets ($1/k_{L,W} = 5(1/mk_{L,O})$). For the current work, the fitting coefficient corresponding to Susanti's original correlation was 4.54, being about 1.7 times of 2.6. Such difference is because much smaller flow rates ($Q_W = Q_O = 0.04\text{--}0.17$ mL/min) and a larger PTFE tube (inner diameter 0.8 mm) were applied in their work. Such time-related k_L was also observed in reactive extractions where mass transfer resistance was located in the dispersed droplet side [29,30].

So far, we have demonstrated that the competition between convection and diffusion determined the relation between the volumetric mass transfer coefficient and the residence time. When governed by internal convection (typically within continuous slug), $k_L a$ could be well predicted based on the separate contributions from bubble caps and liquid film, which is independent of residence time. When mass

Fig. 15. Comparison of the experimental and predicted values of mass transfer coefficient k_L under liquid-liquid slug flow in the hydrophobic capillary.

transfer resistance was located in dispersed droplets, the effect of diffusion was not negligible anymore. In this case, $k_L a$ was found to decrease along the channel, and k_L could be predicted by the classic penetration theory and a coefficient characterizing the relative contribution of convection therein. In conclusion, the mass transfer rate under convection dominance is more stable and potentially faster than that under significant influence of diffusion. Therefore, special care should be taken in the latter case, especially for fast reactions with a highly exothermic feature. Because prominent conversion and heat emission are expected to happen in the inlet area, which requires large heat transport capacity and high safety index. If the liquid film was active, it is better to shift the resistant phase into the continuous phase, in order to facilitate both the overall reactor performance and operating stability. Additionally, physical properties such as wetting ability, the viscosities of employed phases (imposing viscous force on droplet surface) and operating conditions (e.g., channel dimensions, flow rates, etc.) also play important roles on the results of such competition [51,59,62,63]. These factors will be closely investigated in our future work.

4. Conclusion

The slug flow microreactors have received numerous investigations in recent decades towards the multiphase systems, due to its precise controllability and fast transport rate that is critical for highly exothermic and/or mass-transfer-sensitive reactions. Under sufficient convection, the overall volumetric mass transfer coefficient $k_L a$ followed its physical definition that only depends on the flow conditions. However, this is not always true in practical operations owing to the competition between convection and diffusion, leading to a decreasing $k_L a$ along the channel. In order to reveal the effect of such competition on mass transfer performance in both continuous slugs and dispersed droplets, we employed the colorimetric oxidation-reduction of resazurin with oxygen, where the mass transfer resistance always located in the aqueous phase. Accordingly, two sets of experiments were conducted: (1) air-water and *n*-octane-water (air and *n*-octane served as oxygen sources) slug flows in a hydrophilic glass microreactor and (2) *n*-octane-water slug flow in a hydrophobic PTFE capillary. Distinct mass transfer features were observed in these two systems:

- Within the glass microreactor, $k_L a$ values under fixed flow rates were nearly constant along the main channel, due to the sufficient convection characterized by the strong internal circulation and/or the leakage flow. In detail, two distribution patterns of the transferred oxygen in continuous slugs were observed: (1) mal-

distribution pattern (under $Ce < 0.07$ and $Re < 50$) where the transferred oxygen was enriched at the lower half slug and well mixed within the frame of corresponding circulation loops; (2) even-distribution pattern (under $Ce > 0.17$ and $Re > 70$), where aforementioned concentration difference within the slug disappeared and a strong forward leakage flow between adjacent slugs occurred. Though such difference in mixing patterns, stagnant regions were not observed in either case, confirming the dominance of convection. Consequently, the corresponding k_La could be well predicted by estimating separate contributions from the slug bulk and the liquid film (Eq. (4)). Additionally, the mass transfer contribution from the bubble/droplet formation stages followed a negative exponential correlation of residence time (Fig. 7), while that in the gas-liquid system was smaller than that in liquid-liquid slug flow.

- However, for the liquid-liquid slug flow in the PTFE capillary, k_La values under given operating conditions decreased monotonically along the main channel (i.e., with residence time increasing), because of the significant role of diffusion against convection. This attribution was demonstrated by the fact that the stagnant region within the droplet constituted a prominent part in aqueous droplets. Also, the corresponding proportion was found to increase as the droplet shortened. Thus, the mass transfer coefficient k_L therein was well predicted by the penetration-theory-based model with an additional term (Q_W/Q_O) to illustrate the effect of droplet length to the overall mixing (Eq. (5)).

These contents demonstrated that the competition between convection and diffusion leads to distinct mass transfer characterizations in biphasic slug flow. The mass transfer within slugs is more likely to be dominated by convection, resulting in the near-constant mass transfer rate along channel length; while diffusion in droplets plays a non-negligible role, presenting a decreasing k_La with residence time. Therefore, it is critical to estimate the location of mass transfer resistance for reliable process predictions. From the aspect of applications, such pre-estimation could also guide the dispersion of the resistance phase (either into the continuous or dispersed phase), to maximize the interest from microreactor and readily achieve operating targets. For researches, insights into the convection-diffusion competition particularly within droplets are urgently needed for better understanding and development of robust models and/or theories.

5. Notations

A	m^{-1}	Volumetric interfacial area in the microchannel
A	m^2	Cross-sectional area
C	mol/L	Solute concentration in the aqueous phase
C^*	mol/L	Saturated concentration of solute in the aqueous phase
d_h	m	Hydraulic diameter of the rectangular channel
D	m/s^2	Diffusivity
H	m	Channel height
J	m/s	Superficial velocity
k_L	m/s	Liquid side mass transfer coefficient
Re	–	Reynolds number
T	ms	Time counting during bubble/droplet formation stage
W	m	Channel width
Subscripts		
0	–	Inlet
1	–	Outlet in the focused area
ave	–	Averaged value
C	–	Continuous phase
C	–	Microchannel or capillary
D	–	Dispersed phase
G	–	Gas phase
max	–	Maximum value
norm	–	Normalized value
O	–	Organic phase
tot	–	total
W	–	Aqueous phase
Dimensionless numbers		

Ca	–	Capillary number, compares the viscous and interfacial forces
Ce	–	Comparison between the centrifugal and interfacial forces
Re	–	Reynolds number, compares the inertial and viscous forces
Greek letters		
Γ	Pa·s	Interfacial tension between phases
ΔG	–	Difference in grey values
M	N/m	Viscosity
ρ	kg/m^3	Density
τ	s	residence time of fluid mixtures

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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