Hydrodynamic Shrinkage of Liquid CO₂ Taylor Drops in a Straight Microchannel

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Hydrodynamic shrinkage of liquid CO₂ drops in water under a Taylor flow regime is studied using a straight microchannel (length/width ~ 100). A general form of a mathematical model of the solvent-side mass transfer coefficient (kₘ) is developed first. Based on formulations of the surface area (A) and the volume (V) of a general Taylor drop in a rectangular microchannel, a specific form of kₘ is derived. Drop length and speed are experimentally measured at three specified positions of the straight channel, namely, immediately after drop generation (position 1), the midpoint of the channel (position 2) and the end of the channel (position 3). The reductions of drop length (Lₓ, x = 1, 2, 3) from position 1 to 2 and down to 3 are used to quantify the drop shrinkage. Using the specific model, kₘ is calculated mainly based on Lₓ and drop flowing time (t). Results show that smaller CO₂ drops produced by lower flow rate ratios (Qₜ/COS/Qₜ/H₂O) are generally characterized by higher (nearly three times) kₘ and Sherwood numbers than those produced by higher Qₜ/COS/Qₜ/H₂O, which is essentially attributed to the larger effective portion of the smaller drop contributing in the mass transfer under same levels of the flowing time and the surface-to-volume ratio (~ 10⁻⁴ m⁻¹) of all drops. Based on calculated pressure drops of the segmented flow in microchannel, the Peng-Robinson equation of state (EOS) and initial pressures of drops at the T-junction in experiments, overall pressure drop (∆P) in the straight channel as well as the resulted drop volume change are quantified. ∆P from position 1 to 3 is by average 3.175 kPa with a ~1.6% standard error, which only leads to relative drop volume changes of 0.3‰ to 0.52‰.

I. Introduction

Mass transfer can be found broadly in various physical and chemical processes [1], such as gas absorption (mostly in liquids) [2], liquid evaporation [3], liquid-liquid extraction [4] and, for many cases, chemical reactions [5-7]. Revealed by two prevalent models of mass transfer, i.e., the film model [8] and the penetration model [2] developed from gas-liquid absorptions, molecular diffusion of the solute across the interface and exposure time of the liquid solvent to the solute at the interface are two key factors, apart from the solubility limit of the solute in liquids) [2], liquid evaporation [3], liquid-liquid extraction [4] and, for many cases, chemical reactions [5-7].

Mass transfer based extractions, emulsions and reactions have been probed as well in capillary- and microchannel-based reactors [35-40]. For both gas-liquid and liquid-liquid systems, various flow regimes (e.g., bubbles, drops, slugs, annular and parallel flows) that result from different flow geometries, fluid properties and/or flow
conditions [41-44] are very likely to influence the mass transfer that mainly occurs at the interface [42], though the influence might also be insignificant [45]. Among all flow regimes, Taylor flow (maybe also referred slug, bubble train, segmented or intermittent flow) has become a widely studied one [7,46]. Taylor segments (bubbles or drops) are generally characterized with a Bond number (\(Bo = \Delta \rho g d^2/\sigma\)) smaller than 3.37 and a capsular form whose equivalent diameter is times of the channel (hydrodynamic) diameter. The popularity of Taylor flow in interphase mass transfer studies, as discussed [7,46,47], is mainly due to: (1) the stability and predictability of the flow regime, (2) well-defined hydrodynamic characteristics (e.g., morphology, monodispersity, size, speed, thickness of the thin film that encloses the drop and separates the liquid slugs from one another, etc.), and (3) recirculations within both liquid slugs and drops that could enhance heat and mass transfer [48-50].

Gas-liquid and liquid-liquid systems at Taylor flow regime within microscale devices have been massively studied [7]. Among the fluids, carbon dioxide (\(CO_2\)) has started to be attempted in the past decade (particularly since 2010) with main interests in microscale fluid dynamics and chemical processes. These attempts are usually driven by: (1) the environmental role of \(CO_2\) as one of the major greenhouse gases in climate change, and (2) the physical and chemical properties of \(CO_2\) based on which chemical reactions and material syntheses may be carried out in an efficient as well as a green way [51]. Accordingly, a few mitigation strategies including \(CO_2\) capture and storage (CCS) have been proposed to reduce industrial emissions and to bar atmospheric \(CO_2\) concentrations [52], and dense \(CO_2\) including liquid and supercritical state has been expected for green chemistry [53,54]. Regardless of the motive and the attempt related with \(CO_2\), mass transfer of \(CO_2\) itself in multi-scale processes such as extraction based \(CO_2\) captures, pipeline transports, geological storage and chemical reactions is always a key issue. Different from an immiscible fluid pair (e.g., water-oil), \(CO_2\) together with an aqueous liquid may be a partially miscible one. Driven by a series of mechanisms, e.g., physical absorption (or dissolution), diffusion and reactions with the solvent, \(CO_2\) Taylor bubbles or drops are likely to shrink due to the mass transfer mainly on and across the interface, the magnitude of which depends on the spatial and the temporal scale as well. Sun and Cubaud [55] experimentally studied the dissolution rate of \(CO_2\) bubbles shortly after initial contacts with three liquids (water, ethanol, and methanol) in a flow focusing device and showed that the shrinkage (in terms of bubble length reduction) was almost linear with time. Later, Cubaud et al. [56] focused on \(CO_2\)-water at an extended microchannel length (~10^3 times of channel width) and reported not only \(CO_2\) bubble shrinkage but also a flow regime transition (segmented to bubbly flow) at very much downstream. Also in a microfluidic flow focusing device, \(CO_2\) bubbles experienced a shrinkage-recovery-shrinkage (termed “bubble breathing”) transition subjected to varying temperatures [57]. Detailed studies of \(CO_2\) dissolution and solubility in dimethyl carbonate (DMC) were performed in a microscale device by the same group [58]. A similar strategy for screening \(CO_2\) solubilities in pure and mixed solvents based on bubble shrinkage in a microfluidic device was provided by Lefortier et al. [59]. Using gas \(CO_2\) and sodium dodecyl sulfate (SDS) solution in a flow focusing microfluidic device, Shim et al. [60] reported two dissolution regimes during \(CO_2\) bubble flow, namely, a rapid size decreasing period (~30 ms) and a subsequent equilibrium regime during which gas was exchanged between the bubble and the liquid phase. Moreover, the mass transfer coefficient of gas \(CO_2\) was investigated at a Taylor flow regime in a microchannel and significant shrinkage effects of \(CO_2\) segments were reported [61]. However, none of these studies are related to dense \(CO_2\), and very few literature have reported on the shrinkage effect of dense \(CO_2\) drops or segments, especially in a hydrodynamic scenario.

In this work, liquid \(CO_2\) under a Taylor flow regime is going to be studied in a uniquely fabricated microfluidic device. De-ionized (DI) water is used as the solvent as well as a continuously flowing liquid. A micro T-junction is applied to produce liquid \(CO_2\) Taylor drops. With a long straight microchannel downstream, hydrodynamics and the mass transfer of liquid \(CO_2\) drops in water are probed. In section II, a general mathematical model of the solvent-side mass transfer coefficient (k_s) is developed based on the drop volume change in a hydrodynamic scenario. Based on a detailed geometrical description of a single drop enclosed by thin films in a rectangular microchannel, a specific form of k_s is derived by meticulous formulations of the surface area
and the volume of the drop. In the second part of Section II, an overall pressure drop due to micro-segmented flows in microchannels is considered. With the calculated overall pressure drop, the Peng-Robinson equation of state [62] and the initial CO\textsubscript{2} pressure in the T-junction, the drop volume change subjected to the pressure drop is analyzed. Section III introduces the experimental methodology and procedures and shows an overview of observed liquid CO\textsubscript{2} drops at three specified positions of the channel. In Section IV, experimental results and discussions are given. Section V is a conclusion of our work.

II. Methodology

A. Mathematical model of solvent-side mass transfer coefficient \(k_s\)

A1. A general form of \(k_s\)

In order to formulate the solvent-side mass transfer coefficient \(k_s\) (m/s), a one-dimensional and unsteady flow problem where (pure) solute drops separated by solvent liquid segments flow at a Taylor flow regime in a long straight microchannel is considered. An incompressible flow of the drop and the solvent liquid as well as homogeneous material properties are assumed. In addition, no significant reactions are involved during the mass transfer across the interface. Despite an apparently overall unsteady state, the flow characterized by an intermittency could be deemed steady when an accompanying reference frame is induced relative to the moving drop that makes an ensemble averaging possible [63]. As a solute drop moves at speed \(v_1\) and is characterized by length \(L_1\), as shown in Figure 1, it may exhibit shrinkage in terms of drop length reduction due to the dissolution-diffusion resulted mass transfer across the interface. Thus, the drop length \((L)\) becomes a function of the position \((x)\) along the straight microchannel. Continuous phase slugs behave as solvent for solute drops and presumably maintains a constant flowing speed \((v_c)\) spanning the overall length of the straight channel. The cross section of the microchannel is defined rectangular and its width and depth are denoted by \(W\) (see Figure 1) and \(D\) (not shown in the schematic but deemed perpendicular into paper), respectively.

![Figure 1. Schematic of shrinking drops in the other liquid at a Taylor flow regime in a straight microchannel. \(L_1\) and \(v_1\) indicate drop length and speed at position \(x\) \((x = 1, 2, 3\ldots)\), respectively; \(v_c\) is the superficial flowing speed of the continuous fluid over the cross-section of the microchannel; ‘f’ used in the calculation of \(v_c\) is a frame rate (frames per second, fps) of image acquisition in practice. An overall pressure drop \((\Delta P_t)\) is noted as well.](image)

According to the conservation and a quasi-steady state assumption of the mass transfer, \(k_s\) (m/s) over an infinitesimal time can be defined as

\[
k_s A \Delta C_s = \dot{n}_d,
\]

where \(A\) is the effective mass transfer interfacial area, m\textsuperscript{2}; \(\Delta C_s\) is a concentration difference on the solvent side adjoining the interface that drives the mass transfer, mole/m\textsuperscript{3}; and \(\dot{n}_d\) is the molar flux of the mass transfer, mole/s. \(\dot{n}_d\) can also be concisely defined from the viewpoint of mass transfer, i.e.,
\[ \dot{n}_d = \frac{dn}{dt} = \frac{1}{M} \frac{dm}{dt} = \frac{1}{M} \frac{d(pV)}{dt} = \frac{1}{M} \frac{\rho d(V) + V d(\rho)}{dt}, \]  

(2)

where \( \rho \), \( V \) and \( M \) are the density (kg/m\(^3\)), the volume (m\(^3\)) and the molecular weight (kg/kmol) of the solute drop, respectively. Due to incompressible flow, the density of the solute drop is a constant which is irrelevant to time in a specific hydrodynamic scenario. Therefore, \( d(\rho)/dt \) equals to 0, and equation (2) can be simplified as

\[ \dot{n}_d = \frac{1}{M} \frac{\rho d(V)}{dt}, \]  

(3)

Towards a mathematical model, the solute drop is assigned with a nominal molar concentration \( C_d \) (mol/m\(^3\)) and

\[ C_d = \frac{\rho}{M}. \]  

(4)

Combine equation (3) and (4), we have

\[ \dot{n}_d = C_d \frac{d(V)}{dt}, \]  

(5)

by which the mass transfer is correlated to the solute drop shrinkage in terms of drop volume change over time. Substitute equation (5) to (1) gives

\[ k_s A = \frac{C_d}{\Delta C_s} \frac{d(V)}{\Delta C_s dt}. \]  

(6)

One of the main interests in this problem is the solute drop length reduction, or say, the volume reduction thanks to the diffusion-controlled dissolution in a hydrodynamic circumstance. A sharp interface (thickness \( \sim 0 \)) separating the solute drop from the solvent slug very likely feature an equilibrium concentration in a saturation scenario, where this equilibrium concentration is denoted by \( C_e \) (mol/L). Provided that the mass transfer is a limited one and based on a known hydrodynamic circulating condition near the interface that homogenizes the bulk solvent slug, the bulk of the solvent slug is practically of a zero concentration (i.e., \( C_\infty = 0 \)). The concentration difference \( (C_e - C_\infty) \) on the solvent side forms a driving force for the molar flux. Hence, the concentration difference \( \Delta C \) can be expressed by

\[ \Delta C_s = C_e - 0 = C_e. \]  

(7)

Substitute equation (7) into (6), we have

\[ k_s = \frac{C_d}{A} \frac{d(V)}{\Delta C_s dt}. \]  

(8)

\( C_d \) and \( C_e \) are presumably known as long as fluids are known. \( A \) and \( V \) are overall functions of time. Equation (8) is a general form of \( k_s \) in infinitesimal time during which a constant surface area of the drop still maintains.

A2. A specific form of \( k_s \)

As shown by equation (8), the effective surface area \( (A) \) and the drop volume \( (V) \) of the solute drop need to be determined in order for the mass transfer coefficient. To obtain \( A \) and \( V \) via readily accessible parameters that are either known or measurable, a single Taylor drop is considered in a rectangular microchannel under a three-dimensional (3D) scenario. Figure 2 shows a solute drop flowing a microchannel that has a width \( W \) and a depth \( D \) (\( D \leq W \)). As shown in Figure 2b, 2c and 2d, a thin film (with thickness \( \delta \) at the channel wall and thickness \( \delta' \) at the channel corner) of the continuous fluid enclosing the drop exists between the drop and the channel wall and prevents the drop from contacting the wall. This film results from a wall wettability preference to the continuous fluid over the solute fluid. The drop is characterized with an end-to-end length \( L \) and two principal radii of curvature (i.e., \( R_w \) and \( R_d \)) of its meniscus, see Figure 2b and 2c. \( R_w \) and \( R_d \) can be derived by inducing the contact
angle $\theta_c$ between the drop and the continuous fluid at wall, see Figure 3. Here, $R_w$ is chosen as an example showing how the radii of curvature of the drop meniscus is determined. Focusing on the triangle denoted by a right angle symbol in Figure 3, two geometric equations can be written,

$$R_w \cdot \cos(\pi - \theta_c) = W/2 - \delta,$$

(9)

$$R_w \cdot \sin(\pi - \theta_c) + L_{c,w} = R_w.$$

(10)

Figure 2. Schematics of one single Taylor drop in a rectangular microchannel (width: W, depth: D). (a) A 3D view of the drop in the microchannel; (b) a top view of the drop showing the channel width W, the thickness ($\delta$) of the thin film of the continuous fluid, and the radii of curvature $R_w$ in a projected plane; (c) a side view of the drop showing the drop length L, the channel depth D, and the radii of curvature $R_d$ in a projected plane; (d) A-A sectional view of the drop where the thin film is of thickness $\delta$ at the channel wall and thickness $\delta'$ at channel corners (see the inset); (e) a projected right view of the drop meniscus.

Figure 3. Geometrical descriptions of one single Taylor drop in a microchannel. The ellipse symbolizes the drop. Two horizontal dash lines at the top and the bottom indicate the inner channel wall. The drop is presumably composed of two meniscuses and a main part in the middle. A transitional surface section may exist at between the drop meniscus and the middle part.

After rearranging, $R_w$ and $L_{c,w}$ can be obtained as

$$R_w = \frac{W/2 - \delta}{-\cos \theta_c},$$

(11)

and
\[ L_{c,w} = \frac{W/2 - \delta}{-\cos \theta_c} (1 - \sin \theta_c), \]  
(12)

respectively. Further, the length of the drop main part, i.e., \( L_{m,w} \) (see Figure 3), can be determined from deducing \( 2L_{c,w} \) from the total length \( L \), i.e.,

\[ L_{m,w} = L - 2L_{c,w} = L - \frac{W - 2\delta}{-\cos \theta_c} (1 - \sin \theta_c). \]  
(13)

Next, the surface area and the volume of the drop will be solved based on a three-portion composition assumption of the drop, i.e., two drop meniscuses and one main middle part (see Figure 3). Accordingly, the surface area and the volume of the drop are formulated as

\[ A = 2A_{c,w} + A_{m,w}, \]  
(14)

and

\[ V = 2V_{c,w} + V_{m,w}, \]  
(15)

where \( A_{c,w} \) and \( V_{c,w} \) are the surface area and the volume of the drop cap, \( A_{m,w} \) and \( V_{m,w} \) are those of the middlel part of the drop. The drop cap is approximated one half of a general triaxial ellipsoid whose semi-axes are \((W/2 - \delta), (D/2 - \delta)\) and \(L_{c,w}\), respectively, see Figure 2e and Figure 3. To determine \( A_{c,w} \), an approximation (Thomsen’s formula) proposed by Knud Thomsen \[64\] is applied, i.e.,

\[ A_{c,w} \approx 2\pi \left[ \left( \frac{W}{2} - \delta \right)^p \left( \frac{D}{2} - \delta \right)^p + \left( \frac{W}{2} - \delta \right)^p L_{c,w}^p + \left( \frac{D}{2} - \delta \right)^p L_{c,w}^p \right]^{\frac{1}{p}}, \]  
(16)

the least relative error when \( p \approx 1.6075 \) is within \( \pm 1.061\% \). Moreover, the volume \( V_{c,w} \) is calculated as follows,

\[ V_{c,w} = \frac{4}{3} \pi \left( \frac{W}{2} - \delta \right) \left( \frac{D}{2} - \delta \right) L_{c,w}. \]  
(17)

Prior to calculating \( A_{m,w} \) and \( V_{m,w} \), the perimeter and the area of the cross section of the drop middle part that is perpendicular to the flowing direction (see Figure 2d) need to be determined. By referring to the film thickness at the channel wall and wall corners, as shown in the local enlarged view in Figure 2d, the perimeter and the area of the drop cross section are \( 2(\pi x + W + D - 4\delta - 4x) \) and \( [W D - 2\delta (W + D) - (4 - \pi)x^2 + 4\delta^2] \), respectively, in which \( x = \frac{\delta' - \sqrt{2\delta}}{\sqrt{2} - 1} \). Based on literature results of Taylor bubble (or drop) flows in rectangular capillaries with \( Ca < 10^2 \) \[58,65,66\], the thin film thickness \( \delta \) and \( \delta' \) at the channel wall and the channel corner may be approximated by 0.02W and 0.1W, respectively. Thus \( x \) can be simplified as 0.17W, and the perimeter and the area of the drop cross section are further simplified, respectively, as \( 2(0.774W + D) \) and \( (0.96WD - 0.0632W^2) \). Therefore, the surface area \( A_{m,w} \) and the volume \( V_{m,w} \) of the main middle part of the drop can be written as

\[ A_{m,w} = 2(0.774W + D) \cdot L_{m,w}, \]  
(18)

and

\[ V_{m,w} = (0.96WD - 0.0632W^2) \cdot L_{m,w}. \]  
(19)

Substitute Equation (13) into the above two equations and rearranging \( \delta \) by 0.02W,

\[ A_{m,w} = 2(0.774W + D) \cdot (L + 0.96 \frac{1 - \sin \theta_c}{\cos \theta_c} W), \]  
(20)

and
\[ V_{m,w} = (0.96 WD - 0.0632 W^2) \cdot (L + 0.96 \frac{1 - \sin \theta}{\cos \theta} W). \]  

Similarly, Equation (16) and (17) are specified as follows

\[ A_{c,w} \approx 2\pi \left\{ \frac{(0.24 WD - 0.0096 W^2)^{1.6075}}{3} + \frac{[(0.48 W)^{1.6075} + (0.5D - 0.02 W)^{1.6075}] \cdot (0.48 \frac{1 - \sin \theta}{\cos \theta} W)^{1.6075}}{3} \right\}^{0.6221}, \]  

and

\[ V_{c,w} = 0.32\pi W (0.5D - 0.02W) \cdot 0.96 \frac{1 - \sin \theta}{\cos \theta} W. \]  

Integrate equation (20) - (23) with (14) and (15), the surface area A and the volume V of a drop are formulated as

\[ A = 4\pi \left\{ \frac{(0.24 WD - 0.0096 W^2)^{1.6075}}{3} + \frac{[(0.48 W)^{1.6075} + (0.5D - 0.02 W)^{1.6075}] \cdot (0.48 \frac{1 - \sin \theta}{\cos \theta} W)^{1.6075}}{3} \right\}^{0.6221} + (1.548W + 2D) \cdot (L + 0.96 \frac{1 - \sin \theta}{\cos \theta} W), \]  

and

\[ V = (0.96 WD - 0.0632 W^2) \cdot L + (0.0435 WD + 0.0221 W^2) \cdot \frac{1 - \sin \theta}{\cos \theta} W. \]  

It is necessary to note that a transitional surface section (see Figure 3) from the drop meniscus to the main middle part has not been considered, instead, is incorporated to the middle part of the drop. Thus, the surface area and the volume determined by Equation (24) and (25) are likely to overestimate. The incorporation may only be appropriate when drop length L is relatively larger than the channel width W, thus the transitional area compared with the realistic middle part becomes small. Additionally, the above formulation are generally based on that the volume of the drop middle part is larger than that of the two caps, i.e., \( V_{m,w} > 2V_{c,w} \), thus there exists a critical drop length L (determined by W, D and \( \theta \)) below which Equation (24) and (25) may not be applicable. It can be seen that the surface area and the volume of the flowing drop in a defined channel geometry with involved fluids being known are determinable as long as the drop length L can be measured. The solvent-side mass transfer coefficient, starting from Equation (8), can be further specified as follows

\[
k_s = \frac{1}{A} \frac{C_d}{C_e} \frac{d(V)}{dt} = \frac{1}{A} \frac{C_d}{C_e} (0.96 WD - 0.0632 W^2) \frac{d(L)}{dt}
\]

\[
downarrow
\]

\[
k_s \frac{C_e}{C_d} \frac{1}{(0.96 WD - 0.0632 W^2)} dt = \frac{1}{A} d(L)
\]

\[
downarrow
\]

\[
\int k_s \frac{C_e}{C_d} \frac{1}{(0.96 WD - 0.0632 W^2)} dt = \int \frac{1}{A} d(L) = \frac{1}{(1.548W + 2D)} \int \frac{1}{A} d(A)
\]

\[
downarrow
\]

\[
k_s \frac{C_e}{C_d} \frac{1}{(0.96 WD - 0.0632 W^2)} t = \frac{1}{(1.548W + 2D)} (\ln A)_{A_0} + B
\]
in which B is a constant resulting from the integral. An initial condition (\(A_x = A_0\), at \(t = 0\)) can be applied to determine that \(B = 0\). Thus,

\[
k_s (\text{mm/s}) = \frac{(0.96WD - 0.0632W^2)}{(1.548W + 2D)} \frac{C_d}{C_e} \cdot \frac{1}{t}
\]

\[
k_s = 4\pi \left( \frac{0.24WD - 0.0096W^2}{3} \right)^{1.6075} \frac{0.6221}{1} \left( \frac{0.46^{1 - \sin \theta_{cW}}}{1 - \cos \theta_{cW}} \right)^{1.6075} \left( \frac{0.5D - 0.02W}{3} \right)^{1.6075} \left( \frac{L_s}{4} \right)^{1.6075} \left( \frac{L_t}{4} \right)^{1.6075} + (1.548W + 2D) \cdot (L_0 + 0.96^{1 - \sin \theta_{cW}})
\]

\[
\Delta P_{\text{total}}/L_t = \frac{32\eta_c \bar{V}_c}{(2R_h)^2} \left[ 1 + \frac{8.16 \times 3.34}{32} \frac{1}{L_c^2 A_d \left( \frac{A_e}{Ca_d} + 3.34Ca_d \right)} \right], \quad (27)
\]

where \(L_s\) and \(\Delta P_t\) are the total microchannel length and the total pressure drop over the channel length, respectively. \(\eta_c\) and \(\bar{V}_c\) are the dynamic viscosity and the superficial mean velocity of the continuously flowing slugs, the latter of which can be determined from dividing the total flow rate by the channel cross area. \(R_h\) is the hydrodynamic radius of the microchannel and \(R_h = DW/(D + W)\) for a rectangular one. \(L_c^*\) is a non-dimensional length of the continuously flowing slug, and \(L_c = L_{s,w}/(2R_h)\) in which \(L_{s,w}\) indicates the slug length. In addition, \((L + L_{s,w})\) accounts for the length of a flow unit composed by a drop and a continuous slug. \(A_c\) and \(A_d\) are the channel and the bubble cross sectional area, respectively. \(Ca_d\) is the capillary number calculated on the drops.

Based on the modification of a curvature parameter from 7.16 to 8.16, the applicability of Warnier’s model [68] is further extended in terms of such non-dimensional parameters: \(1.45 \leq \text{Re} \leq 567.59\), \(4.5 \times 10^{-5} \leq \text{Ca} \leq 0.067\), \(0.76 \leq L_c^* \leq 46.83\), \(1.05 \leq L_d^* \leq 14.25\), and liquid-liquid Taylor flows in micro capillaries as well. However, as noted by Warnier et al. [68], the model is partly based on the work of Bretherton [69] and Aussillous and Quéré [70] in determining the pressure drop of a single Taylor bubble. Thus, the model as well as the modified one is unlikely to be applicable to circumstances such as non-axisymmetric channels, non-laminar flows of continuous phase, strong inertia, nor non-ignorable velocity of the thin film that separates the bubble from touching the channel wall.

**B2. Drop volume change subjected to pressure drop**

Since a very general dispersed fluid is considered that might be either a bubble or a droplet surrounded by a continuous liquid in the Taylor flow, it is better to use a more applicable equation of state (EOS) to describe the dispersed fluid rather than a classical ideal gas law. Cubic equations, among other equations, of state in terms of volume have been proposed and developed in the past 140 years to correlate pressure, volume and temperature together for a given quantity of substances within a system, to name a few, the Van der Waals EOS [71], the Redlich-Kwong EOS [72], the Soave-Redlich-Kwong EOS [73], the Peng-Robinson EOS [62], volume-translated...
EOS [74,75] and Patel-Teja EOS [76]. Despite such many cubic EOS, a generic cubic EOS [77] may be written as below

\[
P = \frac{RT}{V-b(T_c)} - \frac{c(T_c)\beta(T_r,\omega)}{V_m[V_m+b(T_c)]+b(T_c)[V_m-b(T_c)]},
\]

in which b, c, d, and e are constants or functions of temperature as well as fluid properties (e.g., acentric factors, critical compressibility factors, etc.); P, V and T are pressure, volume and temperature, respectively; R is the universal gas constant. The first and the second term on the right-hand side of the above equation indicate a repulsion pressure and an attraction pressure, respectively. Among numerous cubic EOS not limited to the above ones, the Soave modified Redlich-Kwong EOS (also called Soave-Redlich-Kwong EOS) and the Peng-Robinson EOS have been the most frequently applied ones in studies related to thermo-physical and vapor-liquid equilibrium (VLE) properties. Moreover, as compared by Peng and Robinson [62] between their calculated vapor pressures of pure substances and equilibrium ratios of mixtures and those calculated by the Soave-Redlich-Kwong EOS, Peng-Robinson EOS provided slightly more accurate agreements with experimental data. Therefore, the Peng-Robinson EOS is chosen to correlate the drop volume change (viz., drop length change) with the pressure drop over the micro channel. The Peng-Robinson EOS is given below

\[
P = \frac{RT}{V_m-b(T_c)} - \frac{c(T_c)\beta(T_r,\omega)}{V_m[V_m+b(T_c)]+b(T_c)[V_m-b(T_c)]},
\]

in which

\[
b(T_c) = 0.07780 \frac{RT_c}{P_c}, \quad c(T_c) = 0.45724 \frac{R^2T_c^2}{P_c},
\]

\[
\beta(T_r,\omega) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2,
\]

where P_c, T_c and V_m are the critical pressure, the critical temperature and the molar volume (V_m: volume/mole), respectively; \(\beta(T_r,\omega)\) is a non-dimensional function of temperature ratio \(T_r = T/T_c\) and an acentric factor \(\omega\) of the specific substance (\(\omega\) for common hydrocarbons and N_2, CO_2, H_2S are referred to the figure 2 in Peng and Robinson’s original paper [62]). If temperature (T) is a constant, equation (29) for a known fluid becomes an equation with two unknown variables, i.e., P and V_m. Furthermore, two such equations may be available at the starting and the ending point of the straight channel, and an equation set including these two equations can be obtained as follows

\[
\begin{align*}
P_0 &= \frac{RT}{V_{m0}-b(T_c)} - \frac{c(T_c)\beta(T_r,\omega)}{V_{m0}V_{m0}+b(T_c)V_{m0}-b(T_c)}; \\
P_t &= \frac{RT}{V_{mt}-b(T_c)} - \frac{c(T_c)\beta(T_r,\omega)}{V_{mt}V_{mt}+b(T_c)V_{mt}-b(T_c)}, \quad \text{and} \\
\Delta P_t &= (P_0 - \frac{\sigma \cos \theta_c}{R_h}) - (P_t - \frac{\sigma \cos \theta_c}{R_h}) = P_0 - P_t.
\end{align*}
\]

If \(P_0\) is known in practice, together with the pressure drop determined by equation (27), \(P_t\) at the ending point of the microchannel can be determined and then used to solve out the two unknowns, i.e., \(V_{m0}\) and \(V_{mt}\), where subscript ‘0’ and ‘t’ indicate the parameter at the starting and the ending point, respectively. Based on solved \(V_{m0}\) and \(V_{mt}\), the relative volume change of the drop \(\Delta V/V_0\) due to the pressure decrease can be calculated by

\[
\Delta V/V_0 = N \cdot \Delta V_m/V_0 = N \cdot (V_{mt} - V_{m0})/(N \cdot V_{m0}) = \frac{V_{mt}}{V_{m0}} - 1.
\]

According to equation (27), (31) and (32), an estimated (or directly measured) initial pressure and a (quantitative) knowing of the Taylor flow in the microchannel are required in order to obtain the drop volume change subjected to the pressure decrease. However, such a clear idea of the drop volume change will not be possible without any
experiments or numerical methods. Next, a series of experiments is going to be carried out in which liquid CO\textsubscript{2} and water are used as a drop fluid and a continuous liquid, respectively, in Taylor flow regimes.

### III. Experiments

#### A. Setup

The experimental system (see Figure S1 in SM) introduced in our previous work [78] is applied here to undertake the hydrodynamic dissolution of pressurized Taylor drops in a straight microchannel. In brief, two mechanical syringe pumps (Teledyne Isco 260D and 100DM) are used to deliver two different fluids to the microfluidic system comprised of a self-made non-permanent connector and a silicon-glass microchip. The connector bridges the large-scale stainless steel tubing to the microchip. The fabrication of the microchip is mainly fulfilled by, in sequence, standard photolithography, deep reactive ion etching (DRIE), inlet & outlet drilling, anodic bonding of silicon and glass wafer, and dicing (of bonded wafers) into a final rectangular shape (74 × 44 × 1.2 mm\textsuperscript{3}). As shown by Figure 4, a micro T-junction in the microchip is applied to produce Taylor drops in the microchannel. In particular, liquid carbon dioxide (purity 99.9%, Praxair Canada) is used as a dispersed fluid which is injected at constant flow rates into the side channel of the T-junction; de-ionized (DI) water is used as the continuous liquid flowing at various constant flow rates in the main channel. One specific flow case is characterized by a constant flow rate ratio, i.e., $Q_{\text{LCO}_2}/Q_{\text{H2O}}$. The side channel, main channel as well as the downstream straight microchannel (total length = 14.7 mm) are all characterized by a uniform width (W) of 150 µm and a uniform depth (D) of 100 µm. Although not shown, the further downstream to the end of the straight channel features a 90° turning first and a 55 mm long microchannel which eventually connects to the outlet of the connector. The back pressure of the flowing system is controlled by a back pressure regulator (model EB1ULF1, Equilibar) together with a needle valve. A nitrogen gas tank provides a reference back pressure at the back pressure regulator. However, practical back pressures during experiments are measured by a pressure transducer (Swagelok) installed between the connector and the back pressure regulator. A circulating water bath (Thermo Scientific) for maintaining a constant temperature (i.e., 25°C) of CO\textsubscript{2} from within the pump cylinder, through the stainless steel tubing, up to the microchip is used.

![Figure 4. Schematic of the experimental methodology for investigating liquid CO\textsubscript{2} drops’ shrinkage in a straight microchannel (16 < $L_x/L_t$ < 60, x = 1, 2, 3; W = 150 µm). Drop length $L_x$ is monitored and measured at three positions, i.e., immediately after the drop generation (position 1), at the midpoint of the microchannel length (position 2) and at the end of the microchannel (position 3). Total microchannel length $L_t$ is 14.7 mm.](image)

**Figure 4.** Schematic of the experimental methodology for investigating liquid CO\textsubscript{2} drops’ shrinkage in a straight microchannel (16 < $L_x/L_t$ < 60, x = 1, 2, 3; W = 150 µm). Drop length $L_x$ is monitored and measured at three positions, i.e., immediately after the drop generation (position 1), at the midpoint of the microchannel length (position 2) and at the end of the microchannel (position 3). Total microchannel length $L_t$ is 14.7 mm.

#### B. Measurements

The experimental methodology for studying the dissolution caused Taylor drop shrinkage is schematically introduced in Figure 4. The liquid CO\textsubscript{2} drop at three sequential positions of the straight microchannel, i.e., immediately after the drop generation (position 1), the midpoint of the microchannel (position 2) and the end of
the microchannel (position 3), are visualized by using an upright microscope (BX51, Olympus) combined with a high speed camera (v210, Phantom). Images-stacked videos (3000 fps (frames per second)) are recorded separately at the three positions after a waiting time of 20 minutes, each time when a different \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} \) is applied, in order for a stable flow state. Later, these videos are first cropped into a constant size of 800 × 200 pixels (1 pixel ≈ 2 μm), and then analyzed in Matlab (R2014a, Mathworks, Inc.) by using a series of self-developed Matlab codes based on identifying drops. Drop length (measured from the vertex of the back meniscus to that of the front one of the drop in the flow direction) and drop speed are the two main parameters extracted from the video analysis. Under a given \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} \) at one of the positions, the drop length is measured for all emerging drops in the video, and the averaged value is considered a characteristic drop length, i.e.,

\[
L_x = \frac{1}{N} \sum_{i=1}^{N} L_{i,x}, \quad x = 1, 2 \text{ or } 3,
\]

and the standard deviation \( s_{L_x} \) is calculated by

\[
s_{L_x} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (L_{i,x} - L_x)^2}, \quad x = 1, 2 \text{ or } 3,
\]

where \( N \) is the total number of complete drops that have emerged in the video at position \( x \) (\( x = 1, 2 \text{ or } 3 \)). If one single drop of the \( N \) drops has been presented as a complete one (i.e., both its front and back meniscus are simultaneously visible in the video) from the \( j \)th frame to the \((j + M)\)th frame, an average speed (\( v_{sd} \)) of this drop at this position is determined by

\[
v_{sd} = \frac{1}{M} \sum_{h=1}^{M} v_{h \rightarrow (h+1)},
\]

where \( v_{h \rightarrow (h+1)} \) is the speed of this single drop calculated from two consecutive frames, i.e., the \( h \)th and the \((h+1)\)th frame (\( j \leq h < M \)), as formulated below

\[
v_{h \rightarrow (h+1)} = \frac{\Delta d_{h \rightarrow (h+1)}}{1/\text{fps}},
\]

in which \( \Delta d \) is the drop displacement from the \( h \)th and the \((h+1)\)th frame. Based on \( v_{sd} \), of one single drop, drop speed \( v_x \) by averaging on all the drops is considered a characteristic speed, which is calculated as follows,

\[
v_x = \frac{1}{N} \sum_{i=1}^{N} (v_{sd})_{i,x}, \quad x = 1, 2 \text{ or } 3,
\]

and the standard deviation \( s_{v_x} \) is determined by

\[
s_{v_x} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} [(v_{sd})_{i,x} - v_x]^2}, \quad x = 1, 2 \text{ or } 3,
\]

C. Observations

Figure 5 provides an overview of all liquid CO₂ drops under Taylor flow regime at the specified three positions of the straight microchannel for a total of nine flow rate conditions. Here, the flow rate ratio \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} \) is tuned from 20/80 to 75/25, and \( (Q_{\text{LCO}_2} + Q_{\text{H}_2\text{O}}) \) has been controlled as a constant 100 µL/min. The capillary number \( (Ca_c) \) calculated by the water flow \( (Ca_c = \eta_c v_c/\gamma) \) ranges from \( 8 \times 10^{-4} \) to \( 2.5 \times 10^{-3} \). The viscosity \( (\eta_c = 890 \mu \text{Pa·s}) \) [79] and the interfacial tension \( (\gamma = 31.7 \text{ mN·m}^{-1}) \) [80,81] are referred to 298 K and 65 bar, respectively. Using the same reference, the viscosity of liquid CO₂ in our work is around 58 µPa·s, thus a viscosity ratio \( (\eta_c/\eta_l) \) of 0.065 is used here. In addition, the Schmidt number \( (Sc_c = \eta_c/(\rho_c D_{dc}) \), where \( \rho_c \) and \( D_{dc} \) are the water density and the CO₂ diffusivity in water, respectively, \) of water is calculated around 593, for which \( D_{dc} \) is approximately \( 1.5 \times 10^{-5} \) m²/s [82]. The superficial velocity of water, i.e., \( v_c \), results from dividing \( Q_{\text{H}_2\text{O}} \) by the cross sectional area (WD) of the channel.
At position 1, liquid CO₂ drop generations are periodic, and the length of the generated drops increases as $Q_{LCO₂}/Q_{H₂O}$ increases from 20/80 to 75/25. At position 2 and 3, CO₂ drops also periodically emerge in the imaging frames, and they flow in from the left side and out on the right side. The drop length and the drop speed, at each of the three positions, are measurable based on the aforementioned methodologies. It is noted that when $Q_{LCO₂}/Q_{H₂O} > 75/25$ a complete drop can not be captured by our imaging methods at position 1, and when $Q_{LCO₂}/Q_{H₂O} < 20/80$ the generation of Taylor drops becomes unstable and non-periodic. Therefore, flow rate conditions characterized by $Q_{LCO₂}/Q_{H₂O}$ beyond these two thresholds are not probed in our work.

![Figure 5](image-url)  
*Figure 5. Snapshots of liquid CO₂ drops at three specified positions in the straight microchannel under various $Q_{LCO₂}/Q_{H₂O}$. The scale bar for all images is 150 µm. The image video at position 1 for $Q_{LCO₂}/Q_{H₂O} = 75/25$ results from combining two images in an end-to-end way for showing both the T-junction and a completely generated drop.*

### IV. Results and discussions

#### A. Size of the generated liquid CO₂ drop

The length ($L_1$) of the generated liquid CO₂ drop at the micro T-junction has been measured and normalized by the microchannel width ($W$). Normalized drop lengths (i.e., $L_1/W$) are plotted against the $Q_{LCO₂}/Q_{H₂O}$ of the investigated cases, as shown in Figure 6a.
Figure 6. (a) Non-dimensional lengths ($L_i/W$) of generated liquid CO$_2$ drops at the micro T-junction under various $Q_{LCO2}/Q_{H2O}$; (b) Lengths of the liquid CO$_2$ drops at the three positions ($x = 1$, 2 and 3) under various $Q_{LCO2}/Q_{H2O}$. Each error bar indicates one standard deviation of the mean drop length (i.e., the data point).

The drop length increases from around 1.5W to 6.3W when $Q_{LCO2}/Q_{H2O}$ ascends from 0.25 to 3. These data points are fitted with a method analogous to that having been applied in our previous work [78], i.e., a linear relation between $L_i/W$ and $Q_{LCO2}/Q_{H2O}$ (i.e., the ratio defined by the flow rate of the dispersed fluid to that of the continuous fluid). The fitting line, $L_1/W = 1.15 + 1.79$($Q_{LCO2}/Q_{H2O}$), is shown in Figure 6, which is characterized by an adjusted R-squared of 0.97. The Y-intercept is approximately 1 with a 15% deviation and the slope is 1.79 that is much larger than 1. The factor underlying the slope is related to the squeezing-elongating stage within a period of the drop generation, which has been elucidated previously [78]. The fitting, on the other hand, suggests that distinctly sized Taylor drops in terms of non-dimensional drop length can be produced by simply tuning the applied flow rate ratio in a constant micro T-junction device. However, there should exist an upper limit of $Q_{LCO2}/Q_{H2O}$ beyond which Taylor flow starts to vanish and co-flow regimes occur, as evidenced in our previous work [78]. Drop lengths at the midpoint (position 2) and the ending point (position 3) of the long straight microchannel are measured as well. Figure 6b shows the absolute length of the liquid CO$_2$ drop at the three specified positions under various $Q_{LCO2}/Q_{H2O}$. As shown, for each flow rate condition, there is always a slight decline tendency of the drop length from position 1 to 2 and to 3, and the declines are approximately linear. The drop length tendency qualitatively describe the drop shrinkage which is considered a result of the dissolution-diffusion mechanism across the interface between the CO$_2$ drop and the continuously flowing water.

B. Length reduction of liquid CO$_2$ drops

Detailed drop length reductions are plotted against $Q_{LCO2}/Q_{H2O}$ in Figure 7a. Here, three length reductions, namely, a total length reduction $\Delta L$ ($\Delta L = L_1 - L_3$), a first length reduction $\Delta L_1$ ($\Delta L_1 = L_1 - L_2$), and a second length reduction $\Delta L_2$ ($\Delta L_2 = L_2 - L_3$) are calculated and shown. The scattering data points of respective length reductions are linearly fitted by keeping the slopes as zeros. The mean values of drop length reductions $\Delta L$, $\Delta L_1$ and $\Delta L_2$ are 24.35 µm, 16.52 µm and 7.83 µm, respectively. Correspondingly, the standard errors of these mean drop length reductions are 1.08 µm, 1.71 µm and 1.17 µm, respectively, which are calculated from dividing the standard deviations (see equation 34) by the square root of the sample size (i.e., 9 in our work). These mean drop length reductions may be able to be comprehended in such a way that, regardless of the sizes of the CO$_2$ drops being produced from the T-junction and investigated later in the microchannel, absolute values of $\Delta L$, $\Delta L_1$ and $\Delta L_2$ resulted from the interphase mass transfer from CO$_2$ to water are generally constants, despite of two deviants that occur at $Q_{LCO2}/Q_{H2O} = 45/55$ and $Q_{LCO2}/Q_{H2O} = 65/35$.

To evaluate the total length reductions relative to the original drop length, $\Delta L/L_1$ for all cases are plotted as a function of the flow rate ratios, as shown in Figure 7b. It is obvious that, although the total drop length reductions ($\Delta L$) may be a constant for all cases, $\Delta L/L_1$ is likely to be an exponential decreasing function (whose base is between 0 and 1) of increasing $Q_{LCO2}/Q_{H2O}$. This result is rational in view of the larger surface-to-volume ratios of smaller drops that are produced by lower $Q_{LCO2}/Q_{H2O}$ which further enhance the mass transfer through the interface between CO$_2$ drops and the continuous flowing water. Also plotted in Figure 7b are averaged coefficients of variations (COVs) of the drop lengths at those three positions. Here, the COV of drop lengths at each position is defined by dividing the standard deviation over the mean drop length as follows

$$COV_x = \frac{s_{Lx}}{Lx}, \quad x = 1, 2 \text{ or } 3,$$

where $L_x$ and $s_{Lx}$ are calculated from equation (33) and (34), respectively. The averaged COV as a characteristic of each investigated $Q_{LCO2}/Q_{H2O}$ is obtained from averaging the ones at position 1, 2 and 3, as determined by
\[ COV_{Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}}} = \frac{1}{3} \sum_{x=1}^{3} \frac{s_{L_x}}{L_x}, \quad x = 1, 2 \text{ or } 3. \]  

(40)

The averaged COVs behave as a measure of the variability extent of the mean drop length for each flow rate condition. For almost all the flow rate conditions, averaged COVs are approximately a constant with a value of 0.029 (± 0.003), and vast majority of them are well below the relative drop length reductions except for \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} = 75/25 \). This comparison, in general, shows that the drop length reductions are beyond the error scopes and can be the real characteristics of drop shrinkage.

Figure 7. (a) Shrinkage of liquid \( \text{CO}_2 \) drops quantified by drop length reductions (\( \Delta L, \Delta L_1 \) and \( \Delta L_2 \)) and linear fitting lines (horizontal) of the three calculated drop length reductions, \( \Delta L (\bullet) \): a total length reduction, \( \Delta L = L_1 - L_3 \); \( \Delta L_1 (\triangleleft) \): a first length reduction, \( \Delta L_1 = L_1 - L_2 \); and \( \Delta L_2 (\bigtriangleup) \): a second length reduction, \( \Delta L_2 = L_2 - L_3 \). Solid line is a fitting line of \( \Delta L \), and a positive and a negative one standard deviation band (dash lines above and below the solid line) of the mean \( \Delta L \) are added for reference. (b) Relative total drop length reductions \( \Delta L/L_1 \) (■) versus averaged coefficients of variations (COVs) of drop lengths (×) at various flow rate ratios.

C. Pressure drop and resulted drop volume change

C1. Total pressure drop \( \Delta P_t \)

With experimentally obtained drop and slug lengths and by revisiting the section II. B, the pressure drop and the drop volume change can be evaluated according to equation (27) and (32). Nevertheless, the length of the continuous slugs needs to be known and an estimate of the initial pressure (\( P_0 \)) at the micro T-junction is required as well in order to determine the pressure drop \( \Delta P_t \). Figure 5, on the other hand, delivers an intuitive scene of the slug between two consecutive drops. However, the case \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} = 20/80 \) is unable to show a complete slug length due to a size limitation of our field of view (1650 µm × 380 µm) in which \( \text{CO}_2 \) drops are prioritized. Detailed water slug lengths, under all other flow conditions, have been measured at each of the three positions and are plotted similarly as for drop lengths, as shown in Figure 8. Almost all the cases except \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} = 30/70 \) are characterized by invariant slug length (relative total slug length increases (\( L_{s3,w} - L_{s1,w} \))/\( L_{s1,w} \) ≤ 0.08), which may be also true for \( Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}} = 30/70 \) considering the error having been introduced by the syringe pump operating at lower flow rates.

Shown by equation (27), \( \Delta P_t \) is inversely proportional to the non-dimensional slug length \( L_{c^*} \). Next we are going to calculate the pressure drops in a further-case scenario by using the nominal minimum slug length among the ones at position 1, 2 and 3, which may introduce somewhat overestimated pressure drops. Apart from \( L_{c^*} \), other parameters on the right-hand side of equation (27) are listed in Table 1 and their physical meanings and determinations are briefly introduced in the table annotations. Based on Table 1 and equation (27), the pressure
drop over the practical total length of the straight microchannel is calculated and has been plotted against $\frac{Q_{\text{LCO2}}}{Q_{\text{H2O}}}$ in Figure 9a. Although there exists a slight decrease of $\Delta P$, subjected to increasing $\frac{Q_{\text{LCO2}}}{Q_{\text{H2O}}}$ from 30/70 to 75/25, the decrease compared to the pressure drop is very insignificant. Variations of $\Delta P$ are within 1.6% of a mean value of $\Delta P = 3175.383$ Pa. Despite a constant $\Delta P$, the decreasing trend of $\Delta P$, subjected to an increasing $\frac{Q_{\text{LCO2}}}{Q_{\text{H2O}}}$ (i.e., a larger CO$_2$ drop length fraction and a smaller water slug length fraction in the entire channel) reflects a dominant role of the water slugs in controlling the pressure drop. Moreover, it is also noticed that the contribution of the second term on the right-hand side of equation (27) (non-dimensional as well) to the pressure drop, comparatively, is almost two orders of magnitude smaller than the water as a continuous fluid.
Table 1. The parameters that are applied to calculate the pressure drops over the total channel length by equation 27.

<table>
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<tr>
<th>Q_{LCO2}/Q_{H2O}</th>
<th>( \eta_c \times 10^6 )</th>
<th>( \bar{v}_c \times 10^3 )</th>
<th>( R_h \times 10^6 )</th>
<th>( L_c )</th>
<th>( A_d \times 10^{12} )</th>
<th>( A_c \times 10^{12} )</th>
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<th>( L_t' )</th>
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</table>

1 \( \bar{v}_c \) is a superficial velocity of the water slug at downstream of micro T-junction, calculated by dividing \( Q_{LCO2} + Q_{H2O} \) over the cross section of the microchannel.
2 The capillary number calculated by the CO\(_2\) drops.
3 \( R_h \) is the hydrodynamic radius the microchannel, \( R_h = (1/2)D_h = (1/2)4(WD)/2(W+D) = (WD)/(W+D) \).
4 The cross section area \( (A_d) \) of CO\(_2\) drops is calculated by \( A_d = 0.96WD-0.0632W^2 \), see section A.2.
5 The cross section area \( (A_c) \) of water slugs is calculated by \( A_c = WD \).
6 \( L_c \) is a nominal total length of the straight channel and \( L_c = 15\text{mm} \).
7 \( L_t' \) is a real total length of the channel from experiments, the starting point is the back cap of the first generated drop (in a complete plus shape) at position 1 and the ending point is the front cap of the drop that closely approaches to the end of the channel at position 3.
8 The initial pressure \( P_0 \) at the micro T-junction is estimated by the CO\(_2\) pressure that read from the syringe pump.
Figure 8. Water slug length at the three positions under various $Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}}$. Each error bar indicates one standard deviation of the mean slug length.

Figure 9. (a) Total pressure drops $\Delta P_t$ (Pa) over the practical straight microchannel length and (b) pressure drop gradient $\Delta P_t/L_t$ (Pa/mm, or equivalently, kPa/m), respectively, as a function of flow rate ratio $Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}}$.

As the focus shifts from an absolute pressure drop to a gradient of the pressure drop (i.e., $\Delta P_t/L_t$), as shown by Figure 9b, smaller length fractions of water slugs ($L_c^*$ in Table 1) generally result in a slight increase of $\Delta P_t/L_t$ as $Q_{\text{LCO}_2}/Q_{\text{H}_2\text{O}}$ increases from 30/70 to 75/25, though variations are still subtle. This variation tendency reveals that larger occupations of CO$_2$ drops may lower down overall pressure drops on one hand, but on the other hand, they may lead to a more rapid decline of the pressure drop.

C2. Drop volume change subjected to $\Delta P_t$

Since carbon dioxide (critical temperature $T_c = 304.15$ K and critical pressure $P_c = 7.38$ MPa) is applied as the drop fluid in this study and the temperature during experiments is a room temperature ($T = 298.15$ K, thus $T_r = T/T_c = 0.98$), equation (29) combined with equation (30) can be specified as

$$P = \frac{RT}{V_m - 2.6659 \times 10^{-5} - \frac{4.0183 \times 10^{-1}}{V_m^2 + 5.3318 \times 10^{-5} V_m + 7.107 \times 10^{-10}}}$$

(41)

for which $R = 8.3145$ J/(mol·K) and $\omega = 0.228$ [62,83] of CO$_2$ are used during the specification. In addition, the equation set (31) can also be rewritten as
Note that \( V_{m0}, V_{m1} \) and \( V_{mt} \) in the above equation set have a unit of m\(^3\)/mol. As argued, an estimated initial pressure \( (P_0) \) in addition to the specific pressure decrease is required to evaluate the impact of \( \Delta P_t \) on drop volume change. It is noted in Table 1 that this initial pressure \( P_0 \) at the micro T-junction may be estimated by the CO\(_2\) pressure that reads from the syringe pump, provided that CO\(_2\) under the investigated condition is characterized with much lower viscosities \((58.759 \pm 0.114) \mu\text{Pa}\cdot\text{s}\) compared with water and a much lower flow resistance can result from the pump to the micro T-junction. Estimated initial pressures at the T-junction for all flow conditions are listed in Table 1. By solving the two cubic equations in equation set (42) based on \( P_0 \) and \( P_t \), \( V_{m0} \) and \( V_{mt} \) of CO\(_2\) at position 1 and 3 can be determined, during which only real and rational \((\text{sp}\) solutions are employed. Figure 10a shows the calculated \( V_{m0} \) and \( V_{mt} \) with a unit ‘ml/mol’ \((10^{-6} \text{ m}^3/\text{mol})\). As \( Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} \) increases, the initial pressures \( P_0 \) has also been slightly increased from \( 65.2 \times 10^5 \) Pa to \( 67.1 \times 10^5 \) Pa. Consequently, \( V_{m0} \) shows an overall decline, although subtly, from \( 69.41 \text{ ml/mol} \) to \( 67.59 \text{ ml/mol} \). An almost same tendency arises for \( V_{mt} \). Due to \( \Delta P_t \) (presented in Figure 9a), \( P_t \) always has a slightly smaller \((-3.175 \text{ kPa})\) value than \( P_0 \). The difference between \( P_t \) and \( P_0 \) leads to a very small increase from \( V_{m0} \) to \( V_{mt} \) by 0.03 ml/mol. According to equation (32), relative drop volumes changes \((\Delta V/V_0)\) subjected to \( \Delta P_t \) can be determined via approximating to \([(V_{m0}/V_{mt}) - 1]. \( \Delta V/V_0 \) (scaled by 1000) have been plotted in Figure 10b. It shows that relative drop volumes changes due to the pressure drop are extremely small \((\text{approximately } 0.39\% \text{ to } 0.52\%\)).

Figure 10. (a) Calculated molar volume \( V_{m0} \) (ml/mol) and \( V_{mt} \) (ml/mol) based on \( P_0 \) (see Table 1) and \( \Delta P_t \) (Figure 9a). (b) Relative drop volume changes \( \Delta V/V_0 \) (scaled by 1000) calculated from equation (32).

The relative drop length increases \( \Delta L'/L_0 \) as a result of volume expansions could be equivalent to \( \Delta V/V_0 \) based on an assumption that the drops, despite volume changes, still maintains a constant cross-sectional area. It should be noted that \( \Delta L' \) and \( L_0 \) herein are not pertinent to the real drop, but instead, are equivalent ones to \( \Delta L \) and \( L_1 \) (see Figure 9) by accounting for a cylindrical body of the drop. Therefore, \( \Delta L'/L_0 \) may have same magnitudes as \( \Delta V/V_0 \) does, which then can be compared to \( \Delta L/L_1 \) in Figure 9. Clearly, relative drop length reductions \((\Delta L/L_1)\) dedicated to the dissolution-diffusion of CO\(_2\) in water are almost two orders of magnitude larger than the pressure drop resulted relative drop length expansions. It is thus concluded that the pressure drop due to the flow resistance of water and the existence of CO\(_2\) Taylor drops in the straight channel does not lead to a significant drop size change, especially when this size change is compared with the shrinkage caused by the interfacial dissolution-diffusion of CO\(_2\) in water.
D. Surface-volume ratios of drops

Surface-to-volume ratio is one of the key parameters that controls the mass transfer (particularly the rates) between different substances, especially when it comes to those occurring at interfaces among fluids and/or even solids. In view of the shrinkages of liquid CO$_2$ Taylor drops in this study, surface-volume ratios (S/V) of the drops in the microchannel undoubtedly play a key role. According to the formulations of the drop surface area (A) and the drop volume (V), as shown in equation 24 and 25, respectively, these two parameters can be further specified as follows, given that the channel sizes (width $W = 150 \mu$m and depth $D = 100 \mu$m) are known and a static contact angle $\theta_c (\theta_c = 150^\circ$, see figure 5) may be applicable in the hydrodynamic scenarios,

$$A (\mu$m$^2$) = 432.2L - 522.2,$$  
and

$$V (\mu$m$^3$) = 12978L + 99571.27.$$  

in which $L(\mu$m$)$ is the drop length, and from experiments $L = L_x (x = 1, 2$ and 3). Therefore, surface-volume ratios (S/V, 1/mm) of the drops at position 1, 2 and 3 can be determined from the following equation

$$S/V (1/mm) = \frac{A}{V} \times 10^3 = \frac{432.2L - 522.2}{12978L + 99571.27} \times 10^3.$$  

Substitute the drop length $L$ (the ones shown in Figure 6b) into equation 45, the surface-volume ratio (S/V) at position 1, 2 and 3 at all the investigated flow rate ratios can be calculated, and the calculated values of S/V are shown in Figure 11. For smaller CO$_2$ drops resulted from lower $Q_{LCO2}/Q_{H2O}$, their surface-volume ratios are generally slightly smaller than those of the drops produced at higher $Q_{LCO2}/Q_{H2O}$. This result is opposite to an intuition that smaller drops might generally possess higher S/V. Quantitatively, the determination of S/V should always take into account the surface area and the volume, in which geometrical morphologies of the Taylor drops with respect to microchannels may be necessary. As a specific drop flows from position 1 to position 2 and down to position 3, it experiences a size reduction in terms of length decrease (see Figure 7a), which also results in a certain extent of decrease of the surface-volume ratio. The S/V decrease due to a size reduction are more notable for the smaller drops which have been produced at $Q_{LCO2}/Q_{H2O} < 1$, however, the S/V differences of the drops generated at $Q_{LCO2}/Q_{H2O} > 1$ among at position 1, 2 and 3 are not so obvious, which is attributed to the long drop lengths (see Figure 7) and relative small length reductions (see Figure 9).

![Figure 11](image_url)

Figure 11. Surface-volume ratios of the CO$_2$ drops at position 1 (S/V-1, squares), position 2 (S/V-2, up triangles) and position 3 (S/V-3, down triangles), respectively. Horizontal line shows a mean S/V of 32.6 mm$^{-1}$ for all drops.

Despite the S/V difference among various drops produced at $Q_{LCO2}/Q_{H2O}$ ranging from 0.25 to 3, as shown in Figure 11, the S/V of all drops can be averaged at $32.6 \pm 0.1$ (1/mm). Given that the S/V of all drops are on a
same level (~10^4 m^(-1)), the relative drop length reduction (ΔL/L_1), as shown in Figure 9, are regarded independent of the S/V here in this study.

**E. Drop speed and drop flowing time**

Equation 26 reveals that the mass transfer between the drop phase and the slug phase is determined by not only the drop length L but also the time scale on which the mass transfer occur. The CO_2 drops certainly take time to travel from position 1 to position 2 and down to position 3; and on the other hand, mass transfer has also been in process within this time period. Therefore, knowledge of the drop speeds in the microchannel from after their generations to the very end of the channel, other than the drop sizes, are required to evaluate the mass transfer. Based on the experimental methodologies discussed in section III.B (shown by equation 35 to 38), the drop speed at position 1 (v-1), position 2 (v-2) and position 3 (v-3) has been measured from the experiment and plotted in Figure 12a against to the corresponding Q_{LCO2}/Q_{H2O}. In addition, a horizontal dash line is added in the figure which shows a constant superficial velocity (v_{Total}) calculated from dividing the constant total flow rates (Q_{LCO2} + Q_{H2O}) over the cross sectional area of the channel, i.e., v_{Total} = (Q_{LCO2} + Q_{H2O})/A. v_{Total} is introduced here for a purpose of comparison with the experimentally measured drop speeds.

When Q_{LCO2}/Q_{H2O} is below 1, all drop speeds at the three positions are lower than v_{Total} (111.1 mm/s); however, for one specific flow rate condition, those three drop speeds (i.e., v-1, v-2 and v-3) are very close (differences are less than 3 mm/s) to each other. As can be seen, each drop speed (e.g., v-1) are exactly within the error ranges of the other two speeds (v-2 and v-3). Thus, it is appropriate, in this work, to consider the drop flows as a constant flow speed scenario when Q_{LCO2}/Q_{H2O} is constant and below 1, and an averaged drop speed from the three drop speeds will be applied next for such flow rate conditions (Q_{LCO2}/Q_{H2O} < 1). When Q_{LCO2}/Q_{H2O} > 1, v_{Total} always crosses with all the range lines of the measured drop speeds and separates these error bars nearly into two equivalent parts. It can be interpreted that the measured drop speeds, from wherever the drops are measured, are always in the vicinity of v_{Total}. Besides, focusing on any of all the investigated Q_{LCO2}/Q_{H2O}, it is likely that there exists a decreasing tendency from v-1 to v-2 and down to v-3, which are more notable as the considered Q_{LCO2}/Q_{H2O} is widely larger than 1. Analogous to the cases of Q_{LCO2}/Q_{H2O} < 1, averaged drop speeds based on the measured ones at position 1, 2 and 3 are going to be used to determine the flowing time of drops in the straight channel; note that, however, it does not indicate the flow cases of Q_{LCO2}/Q_{H2O} > 1 are constant drop flows.

Based on averaged drop speeds for each Q_{LCO2}/Q_{H2O} as well as the real channel lengths for the drop flows as shown in Table 1, flowing time of the drops, t_{flowing}, in the straight microchannel can be calculated. The averaged drop speed \( \bar{v} \) is determined as follows

\[
\bar{v} \text{ (mm/s)} = \frac{1}{3} \sum v_x, \ x = 1, 2, \text{ and } 3
\]

and the corresponding standard deviation of \( \bar{v} \), \( \sigma_{\bar{v}} \), can be calculated based on an error propagation, as shown below,

\[
\sigma_{\bar{v}} \text{ (mm/s)} = \sqrt{\left(\frac{\partial v}{\partial v_1}\right)^2 \sigma_{v_1}^2 + \left(\frac{\partial v}{\partial v_2}\right)^2 \sigma_{v_2}^2 + \left(\frac{\partial v}{\partial v_3}\right)^2 \sigma_{v_3}^2},
\]

in which the individual standard deviation \( \sigma_{v_x} (x = 1, 2, \text{ and } 3) \) has been determined from experimental measurements and been reflected by the error bars in Figure 12a. Consequently, the flowing time of the CO_2 drop in the straight channel is calculated from below

\[
t_{\text{flowing (ms)}} = \frac{L_{\text{c}}}{\bar{v}} \times 10^3,
\]
where $L_{t}^{*}$ (mm) is the real total channel length for the CO$_2$ drops and has been introduced in Table 1. Analogously, the uncertainties of $t_{\text{flowing}}$ characterized by the standard deviation $\sigma_{t_{\text{flowing}}}$ can be quantified as follows

$$\sigma_{t_{\text{flowing}}} = \sqrt{\left(\frac{\partial t_{\text{flowing}}}{\partial \bar{v}}\right)^2 \sigma_{\bar{v}}^2} = 1000 \frac{L_{t}^{*}}{\bar{v}} \sigma_{\bar{v}}. \quad (49)$$

![Graph](image1.png)

Figure 12. (a) Liquid CO$_2$ drop speed at position 1 (v-1, squares), position 2 (v-2, up triangles) and position 3 (v-3, down triangles) under various Q$_{\text{CO}_2}$/Q$_{\text{H}_2\text{O}}$. A dash line added in the figure shows a superficial total flow velocity from dividing the total flow rate ($Q_{\text{Total}} = Q_{\text{CO}_2} + Q_{\text{H}_2\text{O}} = 100 \mu\text{L/min}$) over the cross-sectional area ($A = W \cdot D$) of the microchannel. Error bars show one standard deviation for the corresponding drop speed. The error bar caps for v-1, v-2 and v-3 at one specific flow rate ratio are characterized by their widths (the longest for v-1 and the shortest for v-3) for a differentiation purpose. (b) Flowing time ($t_{\text{flowing}}$) of CO$_2$ drops in the straight channel which are respectively determined by equation (48), as shown by the circles, and based on a superficial total flow velocity $v_{\text{Total}}$ (111.1 mm/s), as shown by the stars.

According to the above two equations, the flowing time of CO$_2$ drops are calculated and plotted in Figure 12b. As a reference, the flowing time calculated based on the superficial total flow velocity $v_{\text{Total}}$ (111.1 mm/s) are also plotted in Figure 12b. As a consequence of a slight decrease of $L_{t}^{*}$ from 14mm to 13.5mm, there is a slight decrease of $t_{\text{flowing}}$ from 127.2 ms to 120 ms when $v_{\text{Total}}$ instead of $\bar{v}$ is applied in equation 48. Apart from $L_{t}^{*}$, $t_{\text{flowing}}$ in Figure 12b (shown by the circles) are subjected to different $\bar{v}$ as well. Generally, the $\bar{v}$ at $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} < 1$ are marginally smaller than those at $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} > 1$, as shown by Figure 12a. Consequently, the flowing time $t_{\text{flowing}}$ calculated at $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} < 1$ are approximately 10 ms longer than those calculated at $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} > 1$, as shown in Figure 12b. Furthermore, as argued previously that $\bar{v}$ may be approximated by $v_{\text{Total}}$ when $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} > 1$, $t_{\text{flowing}}$ may also be approximated by those calculated based on $v_{\text{Total}}$ for such cases despite a slight difference (no larger than 4%) between the two sets of results. By accounting for the error ranges of the calculated $t_{\text{flowing}}$ based on experimentally obtained $\bar{v}$, i.e., the error bars in Figure 12b, a trend line of $t_{\text{flowing}}$ from $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} \sim 0.2$ to $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}} \sim 3$ is added which indicates an inversely proportional development of $t_{\text{flowing}}$ as a result of increasing $Q_{\text{CO}_2}/Q_{\text{H}_2\text{O}}$. This trend well justifies the development of the relative total drop length reduction, i.e., $\Delta L/L_1$, as shown in Figure 9, given that the surface-volume ratios $S/V$ for all drops are on a same level ($10^{-3}$ m$^{-1}$).

**F. Solvent-side mass transfer coefficient $k_s$**

Since the drop length and the flowing time of CO$_2$ drops in the microchannel are available, as reported in previous sections, the solvent-side mass transfer coefficient ($k_s$) can thus be determined based equation (26). The channel width ($W = 150$ µm) and the depth ($D = 100$ µm) are known. A nominal molar concentration ($C_n = \rho_{\text{CO}_2}/M$) of pure CO$_2$, an equilibrium concentration ($C_e \approx 1.27$ mol/L [84,85]) at an assumed sharp interface
(saturated with CO₂ molecules) referred to the pressures listed in table 1, and a constant temperature (T = 298 K) are going to be adopted in our calculations. Moreover, a static contact angle θ₀ = 150° (estimated from Figure 5) between CO₂ drops and water can be applicable as well. Therefore, equation (26) is further specified as follows

\[
k_s = 30.03 \frac{C_d}{c_e} \left( \ln \frac{432.2L_0 - 522.2}{432.2L_x - 522.2} \right) \times \frac{1}{t},
\]

in which \( k_s \) has a unit of \( \mu \text{m/ms} \), or equivalently, \( \text{mm/s} \). In order to determine the nominal molar concentration of CO₂, densities at various initial pressures (\( P_0 \) in Table 1) and a constant temperature (298 K) are used, which are referred to the NIST chemistry webbook [86]. Based on the drop length and the drop flowing time reported in Figure 6b and Figure 12b, respectively, we have calculated the mass transfer coefficients \( k_{s,1-3} \), as shown in Figure 13a. It is noted that the \( k_{s,1-3} \) calculated here is a convective mass transport coefficient [87] accounting for a dynamic fluidic scenario within the solvent slug and local convective vortices in the vicinity of the interface with the solute drop. Given with the CO₂ diffusivity (\( D_{dc} \approx 1.5 \times 10^{-9} \text{ m}^2/\text{s} \) [82]) in water and that a half channel width as a characteristic length (i.e., \( L_{mass} = W/2 \)) for the mass transfer, the Sherwood number (\( Sh = k_{s,1-3}/(D_{dc}/L_{mass}) \)) that compares the relative strength of the convective mass transfer with that of the purely diffusive one can be determined, the magnitude of which is shown in Figure 13b.

![Figure 13](image)

Figure 13. Solvent-side mass transfer coefficients \( k_{s,1-3} \) (a) and Sherwood number (b). Error bar indicates the standard deviation calculated according to error propagation.

Figure 13 shows that a slightly larger mass transfer coefficient \( k_{s,1-3} \) results at a lower \( Q_{LCO_2}/Q_{H2O} \) scenario though a longer flowing time and a slightly lower surface-volume ratio exist for a relatively slow drop flow. Despite the variation for \( t_{flowing} \) and \( S/V \), these two parameters are generally on the same level among different flow cases. As shown by Figure 7a, the absolute shrinkage of all drops in terms of total length reduction (\( \Delta L \)) is fairly constant. Further, the absolute drop volume reduction (\( \Delta V \)) may be constant too in view of a same drop cross section. Back to the Equation (8), the surface area (A) very possibly accounts for the result of \( k_{s,1-3} \). For smaller drops produced by lower \( Q_{LCO_2}/Q_{H2O} \), they are of smaller surface area but still achieve excellent mass transfer compared with longer ones. In fact, the thin liquid film (thickness \( \sim 0.02W \)) close to the channel wall is fluidic stagnant (no flow practically) and could quickly reach saturation when a few solute drops pass by, so it will not contribute to the dissolution anymore in a longer time period and only the front and the back meniscus of each drop are effective regions for the mass transfer. Since the calculation of \( k_{s,1-3} \) accounts for the entire surface area, it better reflects the performance of smaller drops and is impaired by the main part of the longer drops that has not contributed much to the mass transfer. Nevertheless, our experimental work reports a solvent-side mass transfer coefficient of 0.1 ~ 0.3 mm/s between water and liquid CO₂ and shows that a smaller size of the solute drop relative to the solvent may be favorable to the mass transport. A similar trend applies to the Sherwood number (Sh) as well provided that \( D_{dc} \) and \( L_{mass} \) are constants. Revealed by Sh numbers ranging from 4 to 14.8, convections (including local ones on
two sides of the interface and the one in the bulk phase) have dominated over a pure diffusion in controlling the mass transfer. And the relative strength of convection is more profound for the smaller solute drop.

V. Conclusion

In this study, hydrodynamic shrinkage of liquid CO$_2$ drops in a straight microchannel has been investigated, where the liquid CO$_2$ takes a form of flowing Taylor drops and water is applied as a continuous solvent phase that behaves as slugs that separate the CO$_2$ drops. An experimental system introduced in our previous work [78] is utilized in this study. In particular, a micro T-junction with a uniform width (W = 150 µm) and depth (D = 100 µm) fabricated in a silicon/glass microchip is used to produce CO$_2$ drops, in which liquid CO$_2$ is injected from a side channel (perpendicular to the main channel) as a dispersed phase and water as a continuous phase flows in the main channel, respectively. As a result of various flow rate ratios (Q$_{LCO2}$/Q$_{H2O}$), different CO$_2$ drops in terms of non-dimensional drop length (L/W) are produced in the micro T-junction. Drop length (L) and drop speed (V) are measured at three specified positions in downstream straight microchannel, namely, position 1 where the drop is exactly pinched off by water, position 2 which is the midpoint of the total length of the straight channel, and position 3 that is located at the very end of the straight channel. Main results are summarized as follows:

- Non-dimensional length (L/W) of the generated liquid CO$_2$ drops at the T-junction is correlated with Q$_{LCO2}$/Q$_{H2O}$. The correlation is found to be linear but the factor of Q$_{LCO2}$/Q$_{H2O}$ is much larger than 1 (specifically, 1.79), which is consistent with what we have reported previously [78] that is essentially attributed to the squeezing-elongating effect of the interface during drop generation.

- Drop length at position 1 (L$_1$) to 2 (L$_2$) and 3 (L$_3$) shows a decreasing tendency. Detailed drop length reductions are manifested by a total length reduction $\Delta$L ($\Delta$L = L$_1$ – L$_3$), a first length reduction $\Delta$L$_1$ ($\Delta$L$_1$ = L$_1$ – L$_2$), and a second length reduction $\Delta$L$_2$ ($\Delta$L$_2$ = L$_2$ – L$_3$). All length reductions versus Q$_{LCO2}$/Q$_{H2O}$ are approximated constant reductions ($\Delta$L = (24.35 ± 1.08) µm, $\Delta$L$_1$ = (16.52 ± 1.71) um, $\Delta$L$_2$ = (7.83 ± 1.17) um), which indicates the absolute drop shrinkage may be independent of the original drop size. However, relative length reduction $\Delta$L/L$_1$ is different among flow rate conditions. $\Delta$L/L$_1$ decreases from 0.1 to 0.025 as Q$_{LCO2}$/Q$_{H2O}$ increases from 20/80 to 75/25. Based on formulations of drop surface area and volume, surface-volume ratios (S/V) of all drops at the three positions are determined. Generally, average S/V from at position 1, 2 and 3 shows a declining tendency subjected to increasing Q$_{LCO2}$/Q$_{H2O}$. As Q$_{LCO2}$/Q$_{H2O}$ > 1 there is almost no S/V difference among all three position based surface-volume ratios. Overall, S/V for all drops can be averaged at (32.6 ± 0.1) mm$^{-1}$.

- Drop speeds at position 1 (v$_1$), 2 (v$_2$) and 3 (v$_3$) are measured, which are applied to calculate the flowing time ($t_{flowing}$) of CO$_2$ drops in the channel, and as a further step, the mass transfer coefficient. When Q$_{LCO2}$/Q$_{H2O}$ < 1, these three drop speeds are very close and generally lower than a reference flow velocity $v_{Total}$, i.e., a superficial velocity by dividing the total flow rate (Q$_{LCO2}$ + Q$_{H2O}$) over the channel cross section. When Q$_{LCO2}$/Q$_{H2O}$ > 1, drop speed decreases from v$_1$ to v$_2$ and down to v$_3$ but still can be approximated by $v_{Total}$. In order to simplify the calculation of flowing time, an average drop speed ($\bar{v}$) by the three speeds is adopted. Besides, a real channel length instead of the total length dedicated to the drop flow is applied. Due to slightly longer real channel lengths and lower drop speeds, $t_{flowing}$ for Q$_{LCO2}$/Q$_{H2O}$ < 1 are roughly 10 ms longer than those for Q$_{LCO2}$/Q$_{H2O}$ > 1.

- Starting from a general form of mass transfer coefficient $k_s$, a specific form of $k_s$ based on detailed drop surface area and volume by considering microchannel size (width W and depth D), contact angle ($\theta_c$) and drop length L$_x$ ($x = 1, 2, 3$) has been developed. And by introducing the CO2 diffusivity and half channel width as a characteristic length, the Sherwood number is determined based on calculated $k_s$. Generally, lower Q$_{LCO2}$/Q$_{H2O}$ having produced smaller drops result in slightly higher mass transfer coefficients as well as higher Sh numbers, which is essentially attributed to the larger effective portion of the drop contributing in the mass transfer under
same levels of the flowing time \( t_{\text{flowing}} \), and the S/V for all drops (\( \sim 10^4 \text{ m}^{-1} \)). The Sh numbers reveal the dominant roles of convection over pure diffusion in controlling the mass transfer.

- Potential effects of the pressure drops (\( \Delta P \)) due to drop flows in the straight microchannel upon the drop volume have been discussed. Despite a slight decrease (\( \sim 100 \text{ Pa} \)) subjected to increasing \( Q_{\text{LCO}_2}/Q_{\text{H}_2O} \), \( \Delta P \) for all conditions is of a mean value of 3175.4 Pa with a standard error of 1.6%. By inducing the Peng–Robinson EOS [62] and using estimated initial pressures (\( P_0 \)) at the T-junction (from the CO\(_2\) pump), drop volume changes relative to original ones are correlated to molar volumes in the EOS and are quantified. Resulted volume changes are calculated as small quantities (\( \Delta V/V_0: 0.39\% \sim 0.52\% \)).

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